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Lecture-06
Inorganic Soil Components

Welcome friends to this second week of lectures for environmental soil chemistry. And our topic for this week 2 of lectures is inorganic soil components. So, basically we will be discussing about different inorganic components which are present in soil. And so, these are the concepts which we are going to talk about in this week. First of all, we will be talking about Pauling's rules, which are very important for understanding the structure of different minerals.

Then we will be talking about primary and secondary clay minerals and or soil minerals. Then specific surface of soil minerals we will talk about and then we will talk about the surface charge of soil minerals. And then finally, we will be talking about identification of minerals by x-ray diffraction analysis. So, these are the some of the topics, which we will be covering in this week.

And so, let us start from the composition of the soil. Those who have already know about our introductory soil sensor technology course in NPTEL. We have already discussed about the composition of the soil, but let us see again what is the basic composition of the soil. You know that soil is composed of both solid components as well as pore spaces and the solid components are basically occupied by different inorganic and organic matter.

And pore spaces are occupied by water and air interchangeably. The inorganic components of soil basically composed of different primary and secondary minerals and they are basically concentrated in 3 soils separates. For example, sand, silt and clay. So, these are the major 3 soil separates, where these inorganic components are concentrated. And so, if you see the volume wise soil composition you will see that the 50% of the soil volume is occupied by the solid component whereas the 50% of the poor rest 50% pore space is occupied by water.

And air interchangeably and in case of the ideal condition, there will be 25% of air soil air and 25% of soil water and among these 50% inorganic compound will be only 45 compound will be 45% whereas, organic matter which had basically composed of microorganisms, macroorganisms and humors will account for only 5%. So, this is the volumetric composition of soil.

Now, in this in this week, we will be basically discussing or focusing on this 45% inorganic mineral matter, which are very important for soil. So, the first question comes what is a mineral. Remember, a mineral is basically a natural inorganic component with definite physical, chemical and crystalline properties. So, to be qualified as a mineral, a compound has to be a natural inorganic in nature as well as they should have different physical, chemical and crystalline properties.

So, let us move ahead and see what is the major classification of the minerals. Well, we can classify the minerals into primary minerals and secondary minerals okay. So, what is the difference between primary mineral and secondary minerals. So, the minerals which have not been altered chemically, since their deposition and crystallization from the molten lava molten lava are known as the primary minerals.

You know that all the minerals are developed from weathering of the rocks. So, these minerals are primary minerals and basically are composing the rocks. So, they when they do not change their chemical structure and retain their original chemical properties, then we are calling them primary minerals. For example, the most important primary material which are present in the earth's crust quartz, feldspar, and pyroxene, olivine, micas.

So, these are very important the primary mineral and remember that Quartz is the most wide you know, dominant primary mineral followed by feldspar and these primary minerals mainly found in sand and silt fraction. So, these primary minerals basically composed the sand and silt fracture which basically from the skeleton of that soil and the sand and silt fractures are chemically nonreactive or inactive.

Now, when this primary mineral due to different types of chemical processes and other processes changes their chemical structure, then they are called secondary minerals. Now, remember the important soil separate clay is basically composed of these secondary minerals. So, these minerals are basically obtained from weathering of the prime minerals and most important feature is their change of their chemical structure or chemical nature.

Example is Kaolinite, montmorillonite, gibbsite, goethite, and they are mainly found in clay fraction as I have already told. So, again primary minerals are concentrated in the sand and silt fraction and sand and silt fractions basically produces the skeleton of this of the soil whereas second clay minerals, secondary minerals also known as clay minerals, because they composed the clay and these secondary minerals basically formed from the weathering of the primary minerals.

And their chemical structure has been changed and these clay fractions, so clay mineral basically produces are basically composed the flesh of the soil. So, this is the difference. So, these 2 tables basically shows different primary and secondary minerals, which are present in the soil. So, if you see the and also their corresponding chemical formula. So, as you can see from here, the most common primary minerals are quartz which has a primary which is a formula of a SiO2 followed by you know the , feldspar, and muscovite is another important primary mineral then biotids, feldspar, feldspar are of different types of different types like orthoclase feldspar, microcline feldspar, albite.

Then amphiboles, tremolite, pyroxene, among the pyroxene these are basically fair you know and you know there are different types of pyroxene as you can see enstatite, diopside, rudunite, olivine, which is a ferro magnesium mineral, epidote, tubulin, zinc and rutile. All these

are different types of our primary minerals. And these primary minerals you can see in the original composition of the rocks.

Because they are mainly you know the rocks are mainly composed of these primary minerals and unless the chemical nature of these primary minerals change they are not termed as secondary minerals. So, once due to different types of chemical weathering or chemical transformation the nature of the the chemical structure of these components change then they became the secondary minerals.

What are the important secondary minerals clay minerals, clay minerals, some examples are Kaolinite, montmorillonite, vermiculite, chlorite, we will discuss them also, allophone. Allophane is a non crystalline clay mineral, also imogolite, goethite, hematite, then magnemite, ferrihydrite, bohemite, gypside, pyruloside, bernicide and dolomite, calcite, gypsum, jerosite.

All these are different types of secondary minerals and these secondary minerals are basically developed from the primary minimal due to decomposition and weathering processes especially chemical weathering process. So, all these are having specific chemical formula and so, the secondary minerals are again mainly present in clay fraction whereas primary minerals are present in sand and silt fraction.

So, while discussing about the structure of a mineral, the most important thing we have to consider is some are some basically rules, which governs the structure of that mineral. Now, most of the mineral structure in soils are ionically bonded and this structure can be predicted based on Pauling's rules given by Pauling in 1929. This picture shows the famous scientists Linus Pauling, who has developed these rules, which basically shows the structure of meaning of a mineral.

And how they are built off and what are the different conditions they need to satisfy to form a structure. So, we know that there are 2 types of bonding present in mineral structure, one is called ionic and that is covalent. Remember that majority of the mineral structure in soil has ionic bonding and when the bonding in a mineral is principally ionic its structure is fairly simple because the ions then may be regarded as rigid spheres. So, in that case in case of ionic bonding we assume that these you know these ions can be considered as rigid spheres.

We will see in a while, you know, we will see very shortly at the geometry of these rigid spheres is governed by Pauling's rules. So, we will be discussing these rules. So, there are a couple of rules let us talk about them one by one. So, Pauling's rule before before learning about the Pauling's rule, let us discuss about 2 important thing. One is radius ration and another is coordination number.

So, if you can see here radius ration basically is a ratio of a radius of the cations by radius of anion and coordination number is basically the number of nearest anions surrounding the particular cation. So, these two are very important factors while discussing the Pauling's rule number one. So, what rule one says. So, the rule one states that a coordinated polyhedron of an anion is formed about each cation and the cation anion

distance being determined by the radius sum which is basically some of cation and anion radii and the coordination number of the cation is governed by the radius ratio.

So, again a coordinated polyhedron of anion is formed about each cation, when the cation anion distance being determined by the radius sum and the coordination number which is the number of nearest and then surrounding the cation will be governed by the radius ratio. So, what does it actually mean. So, let us see in details.

So, according to the radius, sum of the radius of cations and anions you can see here, the cation anion distance is basically governed by this cation by the summation of their radius. As you can see here, because this is an ionic in nature, this bonding is ionic in nature, we are assuming that this cation and anions are having the rigid sphere like structure. Now, remember that since iron tends to surround themselves with many oppositely charged ion as possible.

Predicting coordination number requires using only the relative size of ions which is expressed as a radius ratio. So, this radius of these cations and anions are very important while determining the coordination number. How we will see. So, again let us come back to coordination number. Coordination number basically depends on the relative size of the ions because the radius ratio, we have already talked about it.

So, if all atoms in a crystal are the same size, then there are 2 ways to pair the atoms to form a crystal structure. So, let us assume that there are 6 atoms and all these atoms are having this similar size. Then there are 2 ways to pair the atoms to form a crystal structure. Now, in this case the maximum number of atoms that can be coordinated around an individual is 12 in this way, if we stack 2 layers, so, in that case we will call it 12 fold coordination.

There are 2 ways that atoms can be packed in a 2 fold 12 fold coordination. There are 2 ways that the atoms can be packed in a 12 fold coordination. And we will see them. So, the first I mean before before discussing those 2 ways, let us discuss another important point that the single layer of atoms of equal size which we have seen in the last slide, if this is a single layer of atom of equal size let us assume this is an A, these atoms are denoted by A, then 2 kinds of voids are present in between these atoms. As you can see this one kind of void and this is another kind of void.

And we are renaming we are we are naming these we are raining naming these as B voids and C voids. So, all these voids are triangular in shape and you can see these B voids are pointing up and the triangles which are pointing down are known as this C voids. So, these 2 types of voids are created when there is a 12 fold coordination with single layer of atoms of equal size.

So, if we then it you know if we have this single layer of atoms of equal size, then this 12 fold coordination can be expressed in 2 ways. We call them closest pack. There are 2 types of packing, one is called HCP, another is called CCP. HCP is the short form of hexagonal closes packing

whereas, the CCP is the short form of cubic closest packing. So, let us first discuss the hexagonal closest packing.

So, if you see here if we add, so, we first add a single layer of similar size ions, which is denoted by A. So, if we add a mixed layer, this is the next layer of atoms. So, that they occupy the spacing of the B voids, if you remember this the B voids. So, you can see these second layer is occupied the space above the B voids and then again we add the next layer of these A atoms.

So, if we can see here this will give you a more clear picture. So, we are having a layer of A atoms and then a layer of B atoms and then again a layer of A atoms and B atoms. So, alternatively they are repeating each other and these B atoms layer at basically place above the B voids, it is not directly placed above the A atoms. So, these type of stacking basically result in a sequence of AB AB AB etc., sometimes we call it ABC also, I am sorry ABA.

So, this type of stalking is known as AB AB or sometime we call it ABA type of stalking also. So, this type of closest packing is referred to as that hexagonal closest packing or HCP. It results in a hexagonal lattice with the C axis oriented perpendicular to the AB AB layers. So, this is one of the way of producing this 12 fold coordination, that is hexagonal closest packing.

Now, let us consider the second scenario. So, first we had these A layers and then we add these B layers on the top of B voids. So, if after adding the layer of B atoms, we place the next layer so that the atoms are occupying the position of the C void. So, there are 2 types of voids B void and C void. So, the second layer is placed over the B void and the third layer is placed over the C void.

And continues the process upwards. We get a stacking sequence that runs ABC ABC ABC. So, in case of HCP, we got a stacking sequence of AB AB or ABA. Whereas, in case of CCP or cubic closest packing, we are getting a stacking pattern of ABC ABC. Just like here you can see this is a A layer of atom, then B layer and then C layer and then from the top we will see the stack layer just like this.

So, this is called the cubic closest packing or CCP. So, this is another way of representing that careful coordination. So, it results in a cubic or isometric lattice with the axis perpendicular to the layers. So, now we have seen that 12 fold coordination, what is a 12 fold coordination, then hexagonal closes packing and cubic closest packing.

So, let us move ahead and see them side by side. Again, this is a ABA hexagonal close pack, as you can see it is a A layer which is which is basically at the below the B layers and then A layer. So it is a repetitive A layer, B layer and A layer is a hexagonal close pack. In case of CCP, it is basically AB and C. So, this is the difference in their structure or stacking arrangement.

So, what is the implication of radius ratio in this structure you know arrangements. Remember that the relative sizes are indicated by the

radius ratio of the coordinating atoms or ions. Now in the crystal structure, we usually look at the cations surrounding by the anions. So the radius ratio is basically defined by Rx by Rz, where the Rx is the radius of the cation and Rz is a radius of the surrounding anions.

So, again, this radius ratio is basically Rx by Rz, where Rx is the radius of the cation whereas Rz is the radius of the surrounding anion. So basically radius issue is again, it is the ratio of you know the ratio of the radius of the cations to the radius of the surrounding anions. Now, since the anions are usually larger here you can see the result is decreasing the values of Rx over Rz as the size of the cation decreases.

So, when the size of the cation decreases obviously this radius ratio further goes down. So, what is the problem in that. So, once this radius ratio goes down due to the decrease of the size of the cations. So, there is some changes. So, if we decrease the size of the cation in such an arrangement, still allowing the surrounding anions to touch each other and touch the cation with decreasing size of the cation, the coordination will first result in 8 anion surrounding the cation. So, earlier we started with 12 you know 12 fold coordination.

Now we are moving towards 8 fold coordination because due to the decrease of this catatonic size, we are now surrounding the cation by only 8 anions as you can see here 1 2 3 4 5 6 7 8. So, this is called a 8 fold coordination or cubic coordination because it is called cubic coordination because the shape of the object is constructed by joining the lines through the center of the larger ions is a cube.

So, now, we have seen how we can change from a 12 fold coordination to 8 fold coordination to get a cubic arrangement. Now, while we discussing these another important aspect we have to discuss is called limiting radius ratio. Now, if the size of the coordinated cation become smaller it will become too small to touch this rounding anions, because you know, when it is becoming too small it may be it may not be able to touch the surrounding cations which are larger in size. So, that there is a term called limiting radius ratio that will occur when Rx by Rz becomes too small.

So, the radius ratio for the limiting condition, often called the no rattle limit, because if the radius ratio becomes too small or smaller than that cutoff value, then the cation will rattle or basically they will you know rattle in this sites. So, that is why there is a specific terminology called no rattle limited. So, as you can see here, there are 4 anions surrounding cation.

And so the condition or these no rattle no rattle limit for these 8 coordination or cubic arrangements can be achieved by using the Pythagorean theorem. So, this limiting radius ratio can be calculated by using this Pythagorean theorem. Whereas these 2 Rx + 2 Rz is the total distance and then it is basically the squared terms of this is a combination of these 2 Rz square this and this distance that is 2 root 2 Rz square. And from there we got an Rx by Rz value of 0.732. So, this ratio that is 0.732 is the cutoff and anything if the radius ratio goes

below 0.732 the cations will be too small or will rattle in its site in its site and the structure will collapse.

And then it has to change to 6 fold coordination. So, this is the implication of limiting radius ratio. So, if the latest issue goes below beyond or goes below a certain limiting rate, you know no rattle limit, then the coordination will coordination will change from one form to another from. So, again this when the radius ratio goes below the 0.732, then the 8 fold coordination will change to 6 fold coordination.

So, we have seen how this 12 fold coordination will change to 8 fold coordination to 6 fold coordination. So, guys, let us wrap up here today, and in the next lecture, we will start from here, and then we will see how other coordination compounds can be achieved by changing these limiting radius ratio. And from there, we will discuss the structure of different clay minerals. Thank you very much.