

Transcriber's Name: Prabhavathi
Environmental Soil Chemistry
Prof. Somsubhra Chakraborty
Agricultural and Food Engineering Department
Indian Institute of Technology-Kharagpur

Lecture-07
Inorganic Soil Components (Contd.)

Welcome friends to this second lecture of our module 2. And in this module we are basically talking about the inorganic soil components. And so, in the last lecture, we have started the discussion about the primary and secondary minerals and then we briefly discuss the difference between the primary and secondary minerals. From there we have learned about we have started about the Pauling's rules.

And we have discussed a couple of Pauling's rules. We have started with the Pauling's rule 1 and we have discussed what is coordination number and then we have learned about the implication of coordination number and how this coordination number basically, you know, governs how many, the cations or anions will be co-exist. So we will be coexisting. So, in this lecture, we will or will start the discussion from where we finished in the last lecture. But to give you a context, let us go back and discuss couple of things from the last lecture.

So that the things will be more clear. So, if we go back to our last couple of slides, which we discussed in our which we have discussed in our last lectures. So, so if we go back a couple of slides back where what we have discussed in our last lecture, we started with the coordination number remember that there is when there is single layer of atoms of equal size, there are 2 types of voids one is void B and another is void C.

So, obviously, the void B has the triangular shape where the triangular triangles are pointing up, and those with the triangles pointing down are known as the C voids. So, as you can see here these are basically B voids and this is a C voids. So, if you see that there are 2 types of arrangements, one is called the hexagonal closes packing and other is cubes close closest packing.

Now, if we add the next layer of atoms. So, let us see that if there is a single layer of atom called A and then we are putting another layer next layer of atoms. So, that they occupy the space of the B voids and then they then we are adding a next layer above the A atoms. So, there will be a repeating layer called the AB AB AB just like this and this type of packing is known as the HCP or hexagonal closest packing, it results in a hexagonal lattice with the c-axis oriented perpendicular to the AB AB layers.

And what is the cubic closest packing, now cubic closest packing if when we start with A layer of atoms and then we stack a B layer of atom and just above the B voids and there is further in another layer of atom which is you know which is stacked over the C voids of the A layer, then there is a repeating layered structure like ABC ABC etc. So, these layering structure is known as the cubic closest packing.

Now also these cubic closest packing or CCP results in a cubic or isometric lattice with the c-axis perpendicular to the layer. So, isometric view means basically 3 dimensional view as you can see from this picture that is a 3 dimensional view where 3 layers are atoms stacked over each other creating this packing. So, we have learned about the hexagonal closes packing and cubic closest packing.

So, the next you know this slide basically shows these 2 different types of packing one is the hexagonal close packed and that is a AB face you know centered cubic. So, from there we have an idea about how these layers are stacked over each other. Now, another important thing which we have discussed in our last lecture is called the radius ratio. Remember, radius which is the relative sizes are basically it is basically the ratio of the radius between the cation and the surrounding anions. So the radius ratio is defined by this R_x and R_z .

And this is R_x is basically the radius of the R_x is basically the radius of the cations whereas the R_z is the radius of the surrounding anion. So, since the anions are usually the larger than they are the larger ions, these results in decreasing values of R_x by R_z as the size of the cation decreases. So, this is called the radius ratio. So, let us go ahead and see, what is a cubic coordination.

So, if we decrease the size of the patters in such an arrangement, we are still allowing for the surrounding anions to touch each other and touch the cation you know with decreasing size of the cations the coordination will first results in 8 surrounding cations as you can see, in this in this picture, it is quite clear that these anion is basically surrounded by these 8, this cation is basically surrounded by these 8 anions.

And this is called a 8 fold coordination or cubic coordination. Now, why it is called cubic coordination or 8 fold coordination because the shape of the objects as you can see the shape of the objects object constructed by drawing line through the centers of the larger ion is a basically cube. So, the largest anions to this anions. So, when you draw the lines through the center of these anions will get a cubic shape. So, that is why it is called the cubic coordination.

So, what is the limiting radius ratio we have discussed is the limiting radius ratio. So, if the size of the coordinated cation becomes smaller it will become too small to touch the surrounding anions. So, obviously, as you can see here, this is the cation which is surrounded by 4 you know 4 anions which are larger in size. So, if the coordinated cation becomes so small that it will barely touch only the surrounding anions.

Then there is a concept called limiting radius ratio. So, that will occur when these R_x by R_z become too small. Now, obviously, the radius ratio of the limiting condition often called the no rattle limit, because if the radius ratio becomes smaller than that low rattle limit then what will happen the cation will be rattle in its site. So, it will be disrupted, the structure will be disrupted. So, let us see how we can calculate this limiting radius ratio.

So, if you see this, if you see this picture it is it will be clear that these are the 4 cations with the radius of R_z . So, the distance between these 2 horizontal lines is basically $2 R_z$ which is basically the combination of their radius and if we consider the R_x as the radius of the cation obviously, the total distance from here to here will be basically $2 R_x$. So, obviously, based on the Pythagoras theory we can see that the $2 R_z + 2 R_x$.

So, basically $2 R_z + 2 R_x$ will be it squared will be basically the square of these $2 R_z$ square. So, basically based on the Pythagorean theorem, these distance the square of this distance will be basically equal to the summation of the square of these 2 terms. So as you can see $2 R_z + 2 R_x$, which is the total distance is basically the summation of these 2 terms squared of these terms.

So if we simplify that, we will get this R_x by R_z value of 0.732. So, these R_x by R_z value of less than 0.732. The cation will be if these R_x by R_z , that means if the radius ratio goes below these value of 0.732, then it will be too small that it will rattle sides and the structure will move you know no longer will be stable and then it will be changing to the 6 fold coordination.

So this is the implication of this no rattle limit. So this is the 6 fold coordination as you can see. Now this is also known as octahedral coordination because this shape, which is you know defined by drawing planes through the center of the larger ions is basically showing a octahedron. So, that is, it is called octahedral coordination. Now, octagonal coordination is stable when the radius ratio is 0.732.

However, but decreasing the radius of the cation further, that is R_x if we go on reducing the value of R_x will eventually reach a limit where again the structure will rattle, the iron will rattle in its sites. So, then, the coordination will change from octahedron coordination to further new coordination. So, let us see how it happens.

So, if we consider the no rattle limit for 6 fold coordination, we will get a similar type of calculation. So, the no rattle limit can be basically determined by looking at the horizontal planes running through the ions level at C and D. So, these are the 2 ions labelled as C and D and based on the again the Pythagorean theorem, we can see that these different that is $2 R_z + R_x$ these line is basically the square of this line is equal to the $2 R_z$ square + 2 you know both basically both of them are the same.

So $2 R_z$ and here also the difference or the summation of the radius of the cations of the anions are $2 R_z$, so $R_z + R_z = 2 R_z$. So basically, it will be getting 2 multiplied by 4 R_z squared. So if we simplify this equation, we will get a value of the radius ratio of 0.414. So, that also shows the no limit for 6 fold coordination. So, if the radius ratio goes below the 0.414 the structure goes into 4 fold coordination.

So earlier it was 6 fold coordination. Now, due to the reduction of the cation size, the cat you know the radius ratio changes radiates radius ratio reduces and ultimately this 6 fold coordination will be converted

to the 4 fold coordination. And why we call it this 4 fold coordination because planes through the center of the larger atoms in this case will form a tetrahedron like structure. So, that is called 4 fold coordination, also known as the tetrahedral coordination.

So, let us see one example. So, you can see here this is a tetrahedral coordination and it is tetrahedral coordination obviously, you know in the center there will be you know the cation which is surrounded by 4 you know 4 anions. So, what is the no rattle limit for 4 fold coordination. So, the no rattle limit of tetrahedral coordination is reached when the radius ratio becomes 0.225.

So, if the radius ratio goes below 0.225, then this 4 fold coordination will no longer be valid or you know there will be a rattling of the cations and as a result of that this 4 fold coordination will convert it into 3 fold coordination and so are known as the or it is known as the triangular coordination. So, for triangular coordination you to remember that the coordination number is 3 that is 3 ions are surrounded by 3 anions are surrounded the you know these the smaller cations.

So, as you can see here these are 3 fold coordination or triangular coordination, where this small cation is basically surrounded by 3 anions larger anions. Obviously, as you can see visually one difference that as we are going from 8 fold coordination to 6 fold coordination to 4 fold coordination to 3 fold coordination you are seeing that the size of the cation is going continuously down.

So, if no rattle limit for this 3 or triangular coordination also will appear at a value of 0.155. So, if we calculate the no rattle limit for this triangular coordination, we will get a value of 0.155. So, if the radius ratio goes below 0.155, then the only way the smaller ion can be coordinated if we get a linear kind of linear kind of combination what you know what do you mean by linear combination.

That means, the 2 of the larger ions larger anions will be the 2 sides of the cations. So, this is called 2 fold coordination also known as a linear coordination. So, as you can see from the 8 fold coordination to 6 fold coordination to 4 fold coordination to 3 fold coordination to 2 fold coordination we are continuously changing based on the reducing radius ratio or in other terms by reducing the size of the cations.

As the reducing the size of the cations we wanted to make sure that the cations are barely touching the surrounding anions and that is why we have calculated this no rattle limit and if it is, if the if the radius ratio goes below that low no rattle limit then it will rattle and then it will be converted to a new coordination number.

So, based on the Pauling's rule I, there are certain limits and you know values of the radius ratio and also the corresponding coordination number and type of this you know coordination you know coordination structure are given in this in this in this table as you can see that when the radius ratio is 1 obviously, we are getting a coordination number of 12 and basically we are getting the hexagonal or cubic closest packing.

And when it is from 1 to 0.732 we are getting a cubic packing and from 0.732 to 0.414 we are getting a 6 fold coordination. The shape is octahedral, from 0.414 to 0.225 with the coordination number is 4 and we are getting a tetrahedral combination. They are tetrahedral shape and then from 0.225 to 0.155 we are getting coordination number of 3 and we are getting a triangular arrangement of the ions.

And finally, when the radius ratio goes below 0.155, then we are getting the 2 fold coordination that and the arrangement will be kind of linear. So, all these different types of packings are presented here as you can see that in case of coordination number 3 where we are seeing it will be basically a triangular as I have mentioned and also in case of coordination number 4 we are seeing a tetrahedral shape.

When the coordination number is 6, we are getting a octahedral shape. And for coordination number 8, we are getting an corners of a cube that means a cubical shape here. And finally, for the you know for the coordination number 12. That is a hexagon or cubic closes packing we are getting a basically corners of cubic octahedral. So, for example if the ionic radii for oxygen anion is basically 0.14 nanometers.

And also the ionic radii for silica cation is 0.039 nanometers. So, obviously, if we consider the silicon oxygen and calculate the radius ratio we will be getting a value of 0.279. So, these 0.279 basically comes in these range that is you know tetrahedral combination or tetrahedral structure where the coordination number is 4, so, basically 4 oxygen anion can surround the silica cation and results in a tetrahedral coordination. So, this is basically the implication of Pauling rule I.

Also we can see here different do you know ion cations and anions and their ionic radii and also their radius ratio and corresponding coordination number. So, one thing is clear that alluminum you know, which is you know, $3+$ alluminum cation exist in either tetrahedral or octahedral coordination with oxygen and depending on its temperature of crystallization, because if the higher the temperature the lower the coordination number it is a thumb rule. So, if there is a higher temperature, then there will be lower coordination number. So, from this Pauling's rule, we can basically identify for each of these cation you know, what will be their coordination number.

Now, let us move to the Pauling's rule II. So, Pauling's rule II says that also known as the electrostatic valency principle. So, it states that in a stable coordination structure, the total strength of the valency bonds, which reach an anion from all neighboring cations is equal to the charge of the anion. So, basically the strength of the anion bond is expressed as these smallest which is basically calculated by a ratio of Z to CN .

And where S is the electrostatic bond strength to each coordinated anion Z is the valency of the cation and CN as you know that is the coordination number. So, in effect that charge or the cation is shared equally among the nearest neighboring atom which is basically very clear from this formula because, the strength of a particular bond can be

calculated by dividing the valency of a particular cation by the coordination number. That means number of surrounding anions.

So, if we divide the if you divide the valency of a particular cation by the number of surrounding anion. So, obviously, the charge of the cation will be shared equally among the nearest neighbor anions. Now, for example, for silica that is in the tetrahedral coordination, the Si bond strength is basically 4 by 4 that is 1, in case of aluminium substitution for silica which will discuss very soon, while we will discuss the isomorphous substitution, you will see that aluminium sometimes substitute the silica in the tetrahedral coordination.

So, in that in that case, the aluminium oxygen bonds strength become 3 by 4 where 3 is basically the valency of the cation. That is alluminum and the that oxygen and coordination number is basically 4. So, we are getting 0.75. So, bond strength is decreasing when you are moving from silica tetrahedra to a tetrahedra where silica is substituted by alluminum. So, for alluminum and octahedral coordination alluminum oxygen bonds strength become 3 by 6 where 3 is the basic the valency of aluminium.

And oxygen coordination will be 6, so, we are getting 0.5. So, the electrostatic attraction of the cation to anions is reduced, if another anon is attracting the cation in another direction. So, if we see the Pauling's rule III, the rule III states the existence of edges and particularly of faces common to the anion polyhedra in a coordinated structure decrease its stability.

So, as we as these different you know, coordinated you know, different, different coordinated polyhedras are sharing their edges, their faces, you know we get a we get a notion that obviously, when they are when they are joining together by sharing their faces, obviously, their stability will be decreasing. So this effect is large for cations with high valency and small coordination number, why it is that because the closer the cation there is unstable the coordination obviously.

When the closer you know the when the cation become closer obviously, there will be electrostatic repulsion as a result of that, there will be there will be basically instability in the structure. So, spatially this type of instability is large when the radius ratio approaches the lower limit of the stability of the polyhedron. So, obviously, the low where the radius ratio is going down that means, the size of the cation is going down and subsequently the valency of the cation is increasing and small coordination number we are getting obviously, there will be chance for you know destabilizing the structure.

So, this is called this is basically the essence of Pauling's rule III. So, if you can see here in this picture obviously, you can see this is a single tetrahedral unit, where the silica is surrounded by 4 oxygen cations. And these sheets of tetrahedral basically will form by sharing their you know, there are 3 ways they can bond together, one is by point to point which is the most stable and other is edge to edge and a third is the face to face. As you can see in these the sheets of tetrahedral are basically linked together by point to point bonding.

So, in case of octahedral unit in case of aluminium let us consider an aluminium octahedral unit, where the central cation is the aluminium which is surrounded by 6 hydroxyl ions giving it you know octagonal shape. At these octahedral shape basically they share their edges. These octahedral share their edges to forming sheets of octahedral which you seem very soon. So, basically with cations of higher valence like silica tetrahedral has point to point bonding and with aluminium there is an edge to edge bonding, okay. So, obviously when there is an edge to edge bonding it will be less stable than that of point to point bonding.

So, you can see there are different types of, you know structure and how they share you know how they link between each other you can see that tetrahedral is the single tetrahedral unit, and they are sharing their coordinates and here you can see they are when they are sharing their edges, this octahedral unit when they are sharing their coordinates, and this is a sharing their edges. And this is a cubic coordination and this is basically sharing their coordinate and sharing their edges.

Remember that when they are sharing their edges the chance of staying you know, destabilization is much more than that of sharing their corners.

Pauling's rule IV, the Pauling's rule IV states in a crystal containing different contain different cations those of high relevancy and small coordination number will basically tend not to share polyhedron elements with each other. So, basically, this is because the electrostatic bond strength for bonds between this cation and this coordinate and anions will be relatively large. So, obviously that says that higher the valency cation.

Higher valency cation tends to stay as far apart from others as possible. Now, remember that if the bond strength is more than half of the charge of the anion, it is unlikely that the anion will have more than one bond to the same cation with the same coordination number. So, this is our power Pauling's rule IV. Now, let us see the last rule which we will discuss today that is Pauling's rule V. Pauling's rule V says the number of essentially different kinds of constitutes in a crystal tends to be small.

So, obviously the constituents here you know by by mention different constituents basically meaning the configurations like tetrahedral and octahedral, the obviously the complex the structure, the higher the potential energy higher potential energy.

And hence instability because you know the substance always tend to be in a state of lowest potential possible potential energy. So, more complex the structure of the crystallographic structure, there is more chance of instability. So, this is you know this is the rule V.

So, guys we have already covered different types of you know now all 5 rules of Pauling's and why we have discussed this Pauling's rule will be more clear when we discuss the structure of clay minerals.

So, before describing the structure of the clay minerals it is important that we discuss the soil silicates you know there are different types of structure which you can see if we classify the soil silicates. First of all call the nesosilicates and nesosilicates is basically built by the single separate silica tetrahedral. One example as you can see, it is Olivine, look at what is the next call sorosilicates, now the sorosilicates is the structure where 2 or more link tetrahedra and giving the formula of either Si_2O_7 or Si_5O_{16} and the example of sorosilicates is here given that is epidote.

Now, inosilicate is basically defined by single or double chain of tetrahedral with the basic structural unit of formula of SiO_3 or Si_4O_{11} , also you can see the example of basically the example of you know, silicate here equals pyroxene. So, this is basically single or you know inosilicates, again it is basically showing the single or double chain tetrahedral. Now next is a cyclosilicates.

Cyclosilicates basically the close ring, a double ring of tetrahedral as you can see example is benitoil. And phyllosilicates, this is the most important thing as far as the soil is concerned, because this is the building block of the clay mineral which is the most reactive one of the most reactive fractions of soils. So, as you can see, the phyllosilicates is basically sheets separated them with the basic formula of Si_2O_5 producing a phylum that means a leaf like structure, that is what is called the phyllosilicates.

And the final leave the final one is called the tectosilicates, which is basically a stable framework of tetrahedra producing a formula of SiO_2 and the example of this tectosilicates is basically feldspars, quartz and the other primary minerals. So, guys, you have seen that we have discussed today in detail about the 5 Pauling's rule and also we have discussed the basic classification of the soil silicates.

In the next lecture, we will start from the you know structure of individual clay minerals, and then we will discuss their individual properties based on their structure. Thank you and let us join in our next lecture. Bye.