# Mineral Resources: Geology, Exploration, Economics and Environment
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## Lecture – 22
## Hydrothermal Processes (Contd.)

Welcome to today's lecture. We made a beginning to understand the magmatic hydrothermal system and the resulting deposit taking the porphyry copper deposits, as the example and we would look at it in little more details. And, so as you have discussed the other deposits are also somehow closely related to these deposits and in the last lecture, we saw that these porphyry copper deposits are specifically associated with felsic magmatic rocks, ranging in composition from granite to granodiorite quartz diorite monzonite. I have been going up to a little more alkaline variety syenite also rarely, if we take the entire class the copper molybdenum gold porphyries in general.

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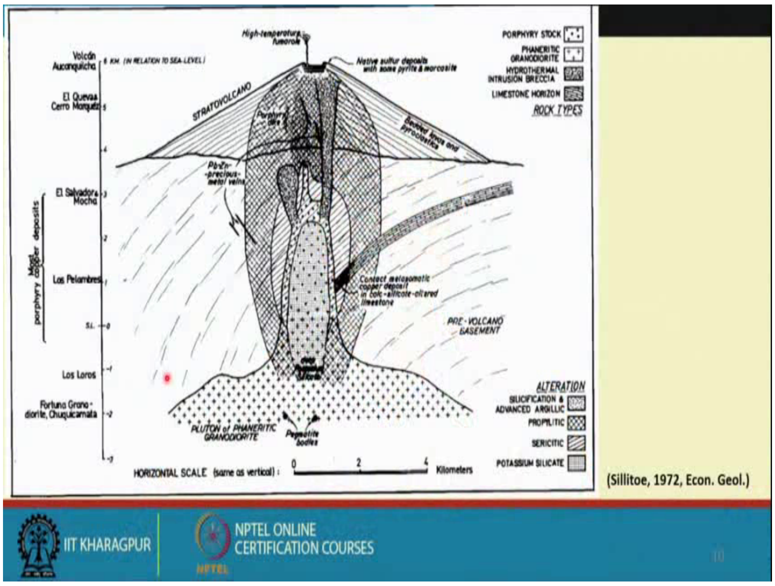

(Sillitoe, 1972, Econ. Geol.)

Let us take a look on this figure which is a model for the occurrence of the porphyry copper deposits, what we see here is, generally what we see that, the porphyry copper deposit is associated with a small plug like body, magmatic body or felsic composition, the range which we have already seen and this small stock is giving rise to a deposit, the quantity of the metals which we get in terms of several thousands, several hundreds of tons even reaching to almost to sometimes say; thousand million tons. So, if we go by a mass balance or this granite being the sole contributor of the metal of course, there is no other possible source. Here, it is the granite, which is the source for the metal, then it does a look like that, such huge mineralization is very unlikely to be resulted by a small magnetic body like this with our understanding on the felsic system, in general and looking into the porphyry system in particular.

This particular model was proposed long back, where it is proposed and what we see is a small stock in the mineralized area, which ever porphyry deposit we visit, it is actually a result of a larger, much larger felsic magmatic system, in the sub crustal level, a deeper levels and this small body is the one, which actually gets separated out of the larger granitic pluton, which was emplaced at a particular depth condition, in the earth's crust.

And, so this is a generalized model, which is given for the porphyry copper deposits. We will discuss about the different alteration zones, but these deposits are essentially characterized by the alteration zones, which surround the mineralized pluton, mineralized plug like body; small plug like body and has a very characteristic porphyritic texture from which the name of the deposit is derived, is porphyry type deposit. They do have a porphyritic texture in the, so having some early formed phenocryst and with ground (Refer Time: 3:54) type of texture and they are associated with many other features. For example, a breccia and then some, it is being, it is including to the country rock, which is by schematically shown here and as we know them, they occur in the continental arch type of setting; Chilean Andes where essentially their stratovolcano type structure.

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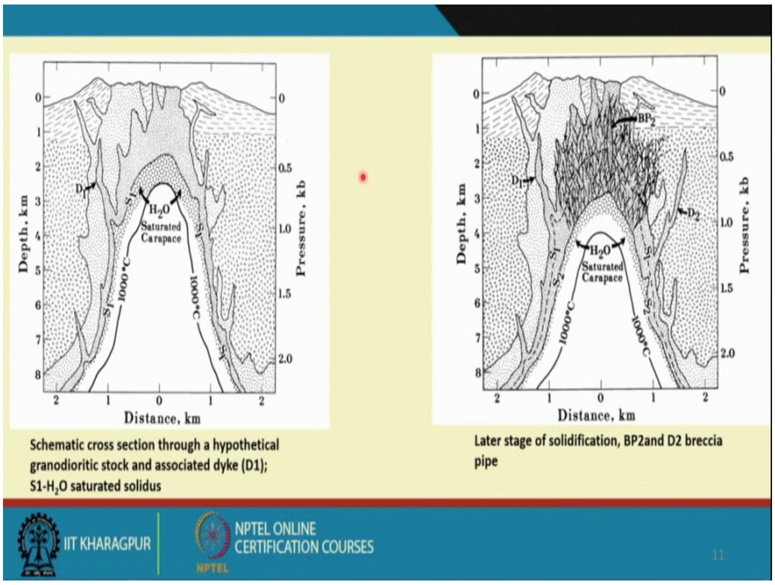

Schematic cross section through a hypothetical granodioritic stock and associated dyke (D1); S1-$H_2O$ saturated solidus

Later stage of solidification, BP2and D2 breccia pipe

Now, these are some of the schematic diagram proposed on, based on the understanding of the felsic system and the way they evolve and the mineralization is resulted. First of all as we know from the very source, from which the paraenetic magma has generated. They are generated from some kind of a veselic amphibolite type of source, which contain water and their structure and the water content could be anything like 2 to 5 weight percent and what is more important is the, when the rocks partially melt the amount of water that is contributed by the partial melt which can be also be calculated by taking some mass balance calculations.

And if we take this particular body which is emplaced in any part of a crust, then during the progress of crystallization this represents a 1000 hypothetical 1000 degree solidus for the system and what is shown here is, there are some smaller injections of this (Refer Time: 05:35) materials in the form of dykes here and this S 1 is representing the water saturated solidus surface. This solidus is equally suppressed here, because of the water content and this particular crystallizing body with crystallization of substance. It’s crystallization of the main with the early crystallizing phases. The residual melt is becoming charged or is concentrated with respect to water, which keeps on in increasing and is accumulating on the top part, which can be called as a water saturated carapace.

Now, here at a later stage of solidification, this water this volatile water along with all the chlorine fluorine and sulphur sulphurous vapour, all are accumulating in the carapace.

They are exerting pressure on the overlying rock and if the in strength of the overlying rock is exceeded, then this results in a network, some deeper region, which is essentially a network of fracture and through which the crystal melt mass along with the residual fluid is these emplaced within the shallow part of the of the of the system and which is exemplified very dense network of fractures, which almost are basically called as the stock work and resulted by the hydro fracturing.

The amount of pressure that is exerted with the percentage of fluid that is accumulated or exerting the pressure can be very well calculated by, from thermodynamic consideration by the change in volume of the fluid with decrease in pressure. And, so, here this also sometimes referred to as a situation, which is this separation of the volatile phase from crystallizing magma with initial crystallization of the anhydrous are very nominally hydrous minerals. This is something called as a retrograde boiling or second boiling and accumulation of the fluid within the carapace region of the crystallizing pluton and exerting pressure, which results in this region, where the small plug like body is emplaced and is also there is brachiation in the rock. So, this gives us a very dense network of fracture and a complicated pattern, but this is actually the region in which the fluid starts, fluid deposits whatever.

So, whatever is the; so, during the melt fluid equilibria metals; like copper which essentially is incompatible during the solid melt interaction, solid melt evolution process, excess incompatible or gets very strongly partitioned into the volatile, which get subs separates exalt out of this crystallizing melt. So, the fluid which exalts from this melt is substantially rich in metals like copper and also gold and they are deposited as the within this region, in a very well defined mineralized part, which we will see here.

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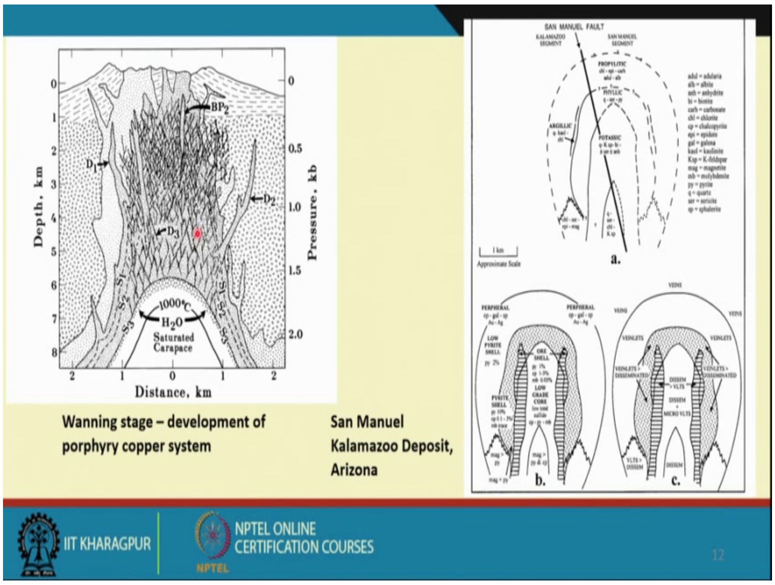

Wanning stage – development of porphyry copper system

San Manuel Kalamazoo Deposit, Arizona

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So, in a later stage where this hydrothermal system is one, in almost coming to the closing stage of the system, there we see there are lots of such dykes and the brecciated regions. And, so, with this general picture, this of evolution, of a magnetic hydrothermal system, which should actually applies to almost all the magmatic system, associated to felsic magmatism will follow a sequence, where there may be a difference here and there based on what is the original or what is the initial conso? The critical parameter is a proposed the very beginning.

The initial water content and the value of water concentration at saturation; that means, the point at which the fluid phase is getting saturated, getting separated or exalt out of the crystallizing melt, they are the critical parameter, the ratio, the value that we get by dividing the original water content, which we can represent as a parameter, which is as a concentration, which we call as a concentration of water, of the say, of the melt, initially when it is initially Cl 0 to a value of water at S.

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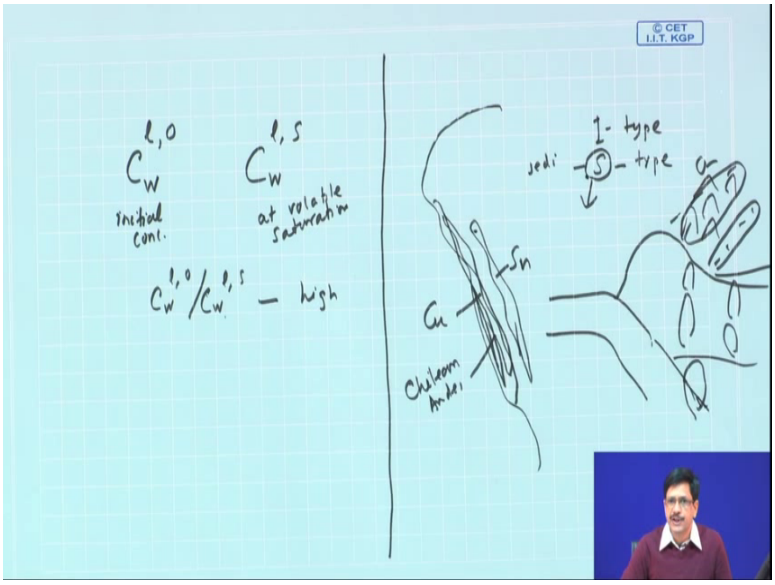

So, this is the initial concentration or initial weight, concentration in water, in terms of weight percent and this value, which could be, it is like the value, at a volatile saturation. So, this ratio Cw l 0 by C w l s is usually high, if the water the origin, the original water content is high and is low and there has been good amount of crystallization of the melt and then it is attaining to water saturation, it also very much is very sensitive to the depth at which it is emplaced and in the context of the porphyry copper deposits. They are generally emplaced at depths corresponding to pressure of almost 500 bars to 2 kilo bars not more than that; that means, almost about 6 7 kilometres to 2 kilometres to 3 kilometres in the below the earth's surface.

So, what results by this process can be schematically shown on this diagram? It is taken from one particular deposit, even this kind of a fault, which is shown at the San Manuel. This is from the San Manuel, Kalamazoo deposit in Arizona and if we look at these two diagrams here, then this is the core representing the small plug like body, which is emplaced and then it is surrounding. So, surrounding that is essentially a zone where there is a low grade mineralization. The chalcopyrite pyrite molybdenite and then there is a rich ore cell part, which contains the maximum concentration of copper and the richest part of the ore body and is surrounded by again a cell, where the spyrite rich, but chalcopyrite is poor and the mineralization dies out and it becomes a country rock. So, here this has a very good correspondence with the alteration, which we will be discussing here. The core part which also is a highest temperature and the fluid has got all the signatures of a directly magmatically derived fluid, with high salinity and very high temperature and this zone is characterized by the kind of mineral alteration, which we call them as potassic, which we will see the reactions; potassic alteration. This is a phyllic alteration, which is dominated by assemblage quartz and sericite and the ore cell is essentially on the richest part of the mineralization coincides, with the boundary of the potassic and the phyllic alteration zones and then there is the arsenic ultrason zone and then this surrounded by a propylitic alteration zone and sometimes we do also have a advance argillic zone which we will be discussing in a short while.

So, taking the felsic, taking the magmatic deposits associated with felsic magmite, felsic rocks, the felsic magmatic system. This is kind of a generalized picture, which can be obtained and is observed in deposits all over the world. There may be some minor variations, here and there sometimes all the alteration zones may not be developed or one later alteration zone, might mask or might imprint. The earlier alteration zone and many variations are possible depending on the local geological conditions, but porphyry copper deposits, all over the world do conform to such kind of a general morphology. So, here since, we at in this particular course, we will be looking at the ore deposits, without getting into details into the ore genesis. We can always see them what exactly the kind of morphology, that is resulted the associated features that helps us in a very meaningful way.

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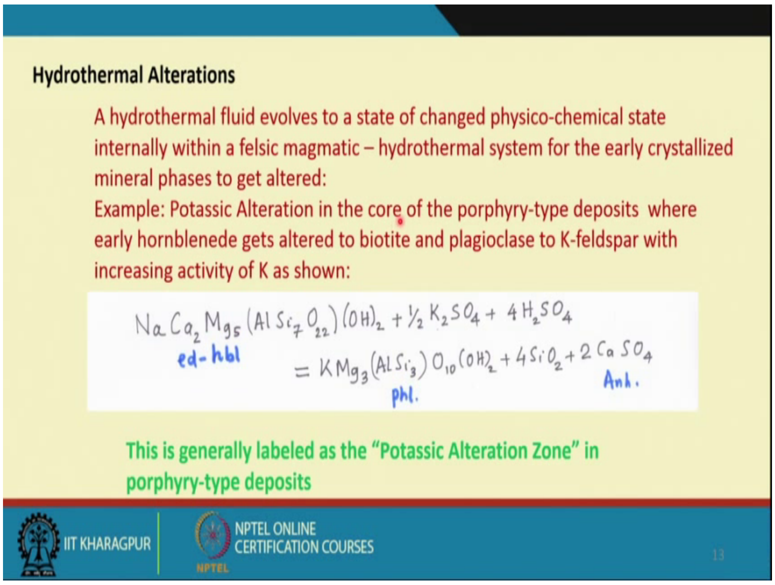

**Hydrothermal Alterations**

A hydrothermal fluid evolves to a state of changed physico-chemical state internally within a felsic magmatic – hydrothermal system for the early crystallized mineral phases to get altered:

Example: Potassic Alteration in the core of the porphyry-type deposits where early hornblenede gets altered to biotite and plagioclase to K-feldspar with increasing activity of K as shown:

$$\underset{\text{ed-hbl}}{NaCa_2Mg_5(AlSi_7O_{22})(OH)_2} + \tfrac{1}{2}K_2SO_4 + 4H_2SO_4 = \underset{\text{phl.}}{KMg_3(AlSi_3)O_{10}(OH)_2} + 4SiO_2 + \underset{\text{Anh.}}{2CaSO_4}$$

This is generally labeled as the "Potassic Alteration Zone" in porphyry-type deposits

So, the hydrothermal alteration zones they one. So, basically the hydrothermal alteration zones we can say that in an evolving system the fluid evolves to such a state that they are that the fluid becomes of the early formed mineral assemblages are out of equilibrium with the changed chemistry of the fluid and this example is the potassic alteration in the core of the porphyry copper deposit, porphyry type deposits, where early hornblende gets altered to biotite and plagioclase to potassic feldspar, plagioclase to potassic feldspar can be simply written by a very simple reaction of addition of potash to a, like an albite plus potash giving rise to potash feldspar, potash soda. So, it very means, very much controlled by the act in the concentration ratios of these two important elements, which is sodium and potassium or we can even write such reactions for calcium.

So, this reaction which is hypothetically, this is an (Refer Time: 15:45) hornblende which is acted upon by the potash rich fluid, which is there in the core of the, with the evolution of the hydrothermal fluid and this fluid is the ph of the fluid is such that we have there in the sulphate stability field. So, this reaction is proposed for conversion of hornblende to bi biotite in a potassic alteration zone typically. So, seen in the core of the porphyry copper deposit, what is to be observed here, is this also gives rise to calcium sulphate, which is anhydride, which is a very ubiquitous in occurrence, in the core zone of the prod of the porphyry copper deposits very widely and this is taken one of the important criteria, for identification of or labelling a depositor, telling a depositor that it is porphyry copper or not.

When it is understood that this most of the sulphur or in the form, where the fluid is in sulphate or most of mainly in the oxidation, in the higher oxidation state, it has also got important bearing in the sense that the metals which were initially dissolved in the melt will not be getting precipitated in this, in the form of sulphides or disseminated sulphide, in that case the result in getting a highly enriched deposit, would not be possible. So, the fluid essentially has to have a higher oxidation state at the beginning. So, that the metals, most of this important metals; like copper, molybdenum, or gold will get partitioned into the vapor phase efficiently. So, that the deposit will result; so, this is the generally, labelled the potassic alteration zone, which is at the core of the porphyry system.

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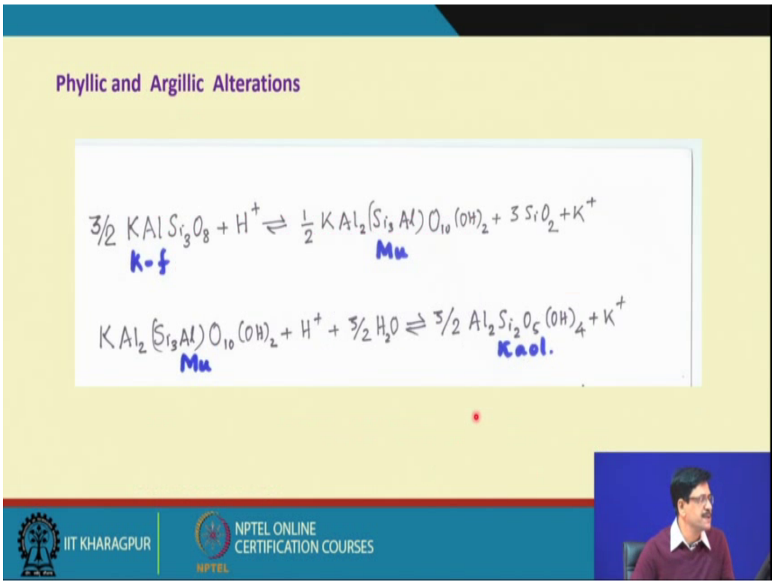

Phyllic and Argillic Alterations

$$\underset{\text{K-f}}{3/2\, KAlSi_3O_8} + H^+ \rightleftharpoons \tfrac{1}{2}\, \underset{\text{Mu}}{KAl_2(Si_3Al)O_{10}(OH)_2} + 3\,SiO_2 + K^+$$

$$\underset{\text{Mu}}{KAl_2(Si_3Al)O_{10}(OH)_2} + H^+ + 3/2\, H_2O \rightleftharpoons 3/2\, \underset{\text{Kaol.}}{Al_2Si_2O_5(OH)_4} + K^+$$

Then when we; as we saw just saw in the diagram, where the concentric cells of the alteration zones, arranged around the centralized mineralized body; we have the Phyllic and Argillic alteration zones, where the Phyllic alteration zone can be represented by the reactions as potash feldspars, acted upon hydrolyzed by H plus ion to give rise to Siri muscovite, which is essentially in the alteration zone. It is set aside the white mica plus silica and live here, some of the potassium ion.

So, it is understandable that it is essentially the ph of the fluid, which is coming to be the controlling factor and 1 into 1 1 of the interesting thing here, is that with the waning stage one; of the important aspect of the waning stage of the magmatic hydro system, like porphyry copper here. Now, once the system is the hydrothermal or the magmatic stage is coming to a close that time. It has enough of opportunity for fluids, low temperature fluids like the meteoric fluid essentially to come, to actually is get infiltrated into the system and interact with the materials to give rise to different types of alterations and the Phyllic. And then when we see the Argillic alterations, where mineral, which is produced here in the say Phyllic zone is muscovite, which is getting again attacked by H plus ion to give rise to kaolinite, which is the index mineral or the mineral, which exemplifies or which characterizes the Argillic alteration zone, around the porphyry copper deposit, following or immediately envelope in the Phyllic alteration zone.

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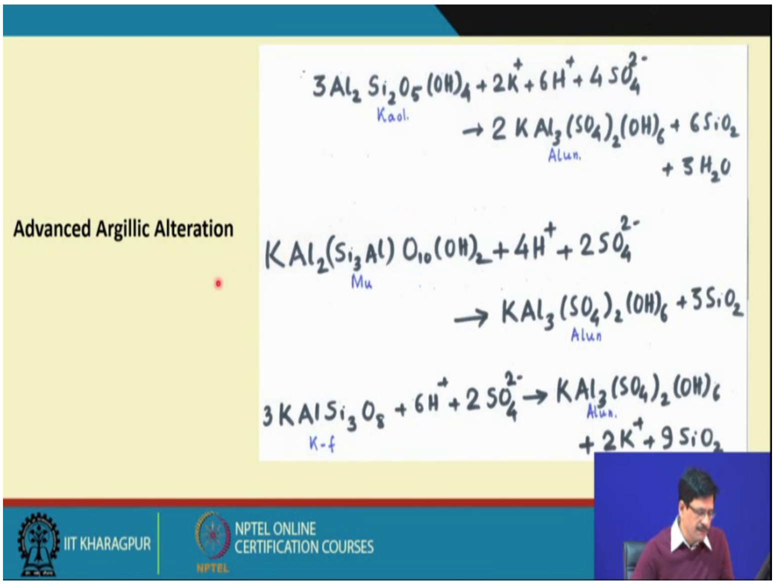

Advanced Argillic Alteration

$$\underset{\text{Kaol.}}{3Al_2Si_2O_5(OH)_4} + 2K^+ + 6H^+ + 4SO_4^{2-} \rightarrow \underset{\text{Alun.}}{2KAl_3(SO_4)_2(OH)_6} + 6SiO_2 + 3H_2O$$

$$\underset{\text{Mu}}{KAl_2(Si_3Al)O_{10}(OH)_2} + 4H^+ + 2SO_4^{2-} \rightarrow \underset{\text{Alun}}{KAl_3(SO_4)_2(OH)_6} + 3SiO_2$$

$$\underset{\text{K-f}}{3KAlSi_3O_8} + 6H^+ + 2SO_4^{2-} \rightarrow \underset{\text{Alun.}}{KAl_3(SO_4)_2(OH)_6} + 2K^+ + 9SiO_2$$

Sometimes, we do get the advanced Argillic alteration, giving rise to minerals like alumnite, where the kaolinite which is produced in the Argillic alteration zone is again acted upon by potash and we have very low acidic, when the ph has gone to much lower value with the abundance of hydrogen ion, this gives rise to alumnite and alumnite is one of the very characteristic mineral associated with the advanced Argillic alteration zone, in porphyry copper deposits. There are several such reactions which can be written. Muscovite can be acted upon by sulphate and high, the very low ph conditions to give alumnite or even potash feldspar, also at very low ph conditions can give rise to alumnite.

So, it does explain to some extent, some of the overlapping situations in which the one alteration zone can penetrate into the other, but in most of the cases the alteration zones can be identifiable.

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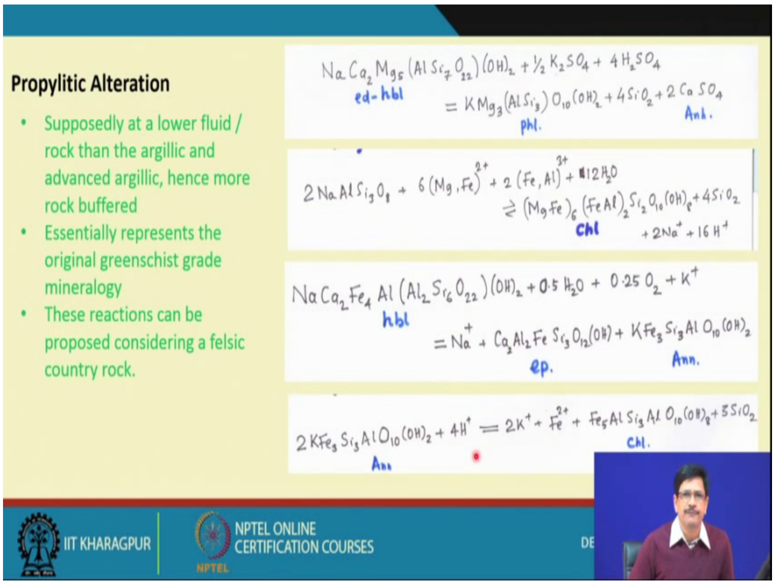

**Propylitic Alteration**

- Supposedly at a lower fluid / rock than the argillic and advanced argillic, hence more rock buffered
- Essentially represents the original greenschist grade mineralogy
- These reactions can be proposed considering a felsic country rock.

$$\underset{\text{ed-hbl}}{NaCa_2Mg_5(AlSi_7O_{22})(OH)_2} + \tfrac{1}{2}K_2SO_4 + 4H_2SO_4 = \underset{\text{phl.}}{KMg_3(AlSi_3)O_{10}(OH)_2} + 4SiO_2 + \underset{\text{Anh.}}{2CaSO_4}$$

$$2NaAlSi_3O_8 + 6(Mg,Fe)^{2+} + 2(Fe,Al)^{3+} + 12H_2O \rightleftharpoons \underset{\text{Chl}}{(MgFe)_6(FeAl)_2Si_2O_{10}(OH)_8} + 4SiO_2 + 2Na^+ + 16H^+$$

$$\underset{\text{hbl}}{NaCa_2Fe_4Al(Al_2Si_6O_{22})(OH)_2} + 0.5H_2O + 0.25O_2 + K^+ = Na^+ + \underset{\text{ep.}}{Ca_2Al_2FeSi_3O_{12}(OH)} + \underset{\text{Ann.}}{KFe_3Si_3AlO_{10}(OH)_2}$$

$$\underset{\text{Ann}}{2KFe_3Si_3AlO_{10}(OH)_2} + 4H^+ = 2K^+ + Fe^{2+} + \underset{\text{Chl.}}{Fe_5AlSi_3AlO_{10}(OH)_8} + 3SiO_2$$

And the alteration zone, which is basically labelled as a Propylitic alteration zone, which is characterized by the presence of biotite and chloride sorry, epidote and chloride that is a little bit of a difference here, because it is a zone which rather indicates rock dominated or low fluid by rock ratio and kind of the original green schist facies, assemblages persistence of the original green schist phases type assemblies in the rock.

So, what essentially we are getting in a system here? The porphyry copper deposits are very much characterized by multiple phases of such intrusions in one particular, if you see the sections of many such deposits, we find that there are many phases of such felsic intrusions in one particular deposit, particular mineralization zone and sometimes it is observed that the latest phase is essentially the productive stage, which is a product of the crystallization evolution of a larger magmatic melt, kinetic magmatic melted depth.

So, the alteration that we get is essentially within this (Refer Time: 21:52) of the felsic country rock which are there or sometimes could be the sediments. So, this alteration the propylitic alteration zone is characterized by presence of biotite and epidote, which we can see that this is a (Refer Time: 22:08) and gets altered to phlogopite as we saw before or a phlogopite kind of biotade. Biotite can be hydrolyzed to give rise to chloride. So, maybe the combination of such kind of reactions will be giving rise to a situation, where we would have epidote and chlorite to be dominant in this alteration zone, which is characteristic of the propylitic alteration zone and it is understood that from potassic zone to the advanced argillic zone, in the propylitic zone the temperature of the fluid is decreasing it is gradually from an original magmatic fluid, which is getting cooled, because with mixing of meteoric fluid and also in terms of the salinity, of the fluid is the higher, is the most in the potassic alteration zone, where the fluid intrusion sometimes shows presence of multiple daughter phases. And the salinity in terms of weight percent NaCl equivalent going to almost 60 65 or 70 in many, studied well, studied porphyry copper deposits, in the western American cordillera.

So, isotopic studies and many other kind of studies done on the porphyry copper deposits, very clearly shows the involvement of magmatic fluid. So, this is the general characteristic of the porphyry copper deposits around the world variations.

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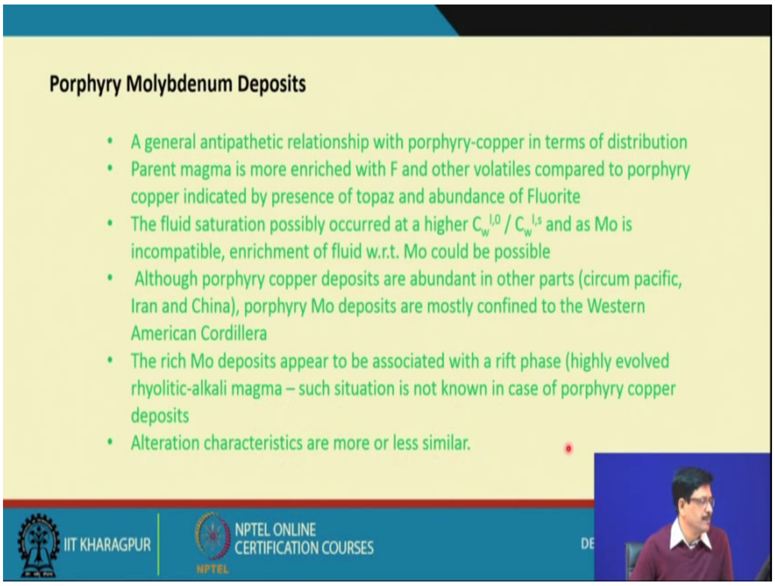

**Porphyry Molybdenum Deposits**

- A general antipathetic relationship with porphyry-copper in terms of distribution
- Parent magma is more enriched with F and other volatiles compared to porphyry copper indicated by presence of topaz and abundance of Fluorite
- The fluid saturation possibly occurred at a higher $C_w^{l,0} / C_w^{l,s}$ and as Mo is incompatible, enrichment of fluid w.r.t. Mo could be possible
- Although porphyry copper deposits are abundant in other parts (circum pacific, Iran and China), porphyry Mo deposits are mostly confined to the Western American Cordillera
- The rich Mo deposits appear to be associated with a rift phase (highly evolved rhyolitic-alkali magma – such situation is not known in case of porphyry copper deposits
- Alteration characteristics are more or less similar.

So, with that in mind if we just try to see what the porphyry molybdenum deposits are. So, these porphyry molybdenum deposits generally do have an antipathetic relations relationship with copper in terms of the distribution the areas like the Chilean Andes or the regions in the West American cordillera where there are there are dominance of porphyry copper deposit we do not see much of molybdenum deposits there the ones which are like the very the example is the climax deposit in Colorado or the this Henderson and climax in Colorado and the there are some such deposits rich deposit of molybdenum which are not associated with or not in very close special association with the porphyry copper deposits, they possibly something which is critical about molybdenum deposits or which exactly was not in very well known.

Although, many of the porphyry copper deposits do have concentrations of molybdenum insignificant quantity. So, here the differences which have been found out in such cases are that the parent magma is more enriched with fluorine and other volatiles. So, it apparently, it looks like that the source, the magmatic rock, which gives rise to porphyry molybdenum deposit, is more felsic in it’s composition and have a very high concentration of the more volatile components like, fluorine and other volatile species. It is indicated by presence of topaz and abundance of fluorite along with the in the alteration zones and mineralized and domains in the porphyry molybdenum deposit and one of the important differences was discussed here, is the critical parameter, which is the ratio of the C w l 0 by C w l s that is the original. The initial water content divided by the water content and saturation is generally, very high in case of molybdenum deposits and is low in case of copper deposit, because of the very inherent, difference between these two elements; molybdenum, copper. Molybdenum is, copper is more compatible than molybdenum in it’s nature although, porphyry copper deposits are abundant in the other parts, say Circum pacific.

So, this is what exactly we have been seeing, that in the Circum pacific region, Iran, China, and many other in the Chilean Andes, these porphyry molybdenum deposits rather rare and mostly confined to the Western American cordillera rich molybdenum deposits appear to be associated with a reef phase, which is actually not very conclusively known in case of the porphyry copper deposit, that the rather poorer or lean molybdenum porphyry. Molybdenum deposits are associated with the magmatic bodies, which are product during the conversion type tectonics settings, where the rich part of the most richest part of the porphyry molybdenum deposit are associated with situation, which more corresponds to a rifting phase where you have highly evolved rhyolitic and alkaline kind of magma which gives rise to porphyry molybdenum deposit, which is not known in the porphyry copper deposit situation; whereas; the alteration characteristics are more or less similar in the two types of deposits.

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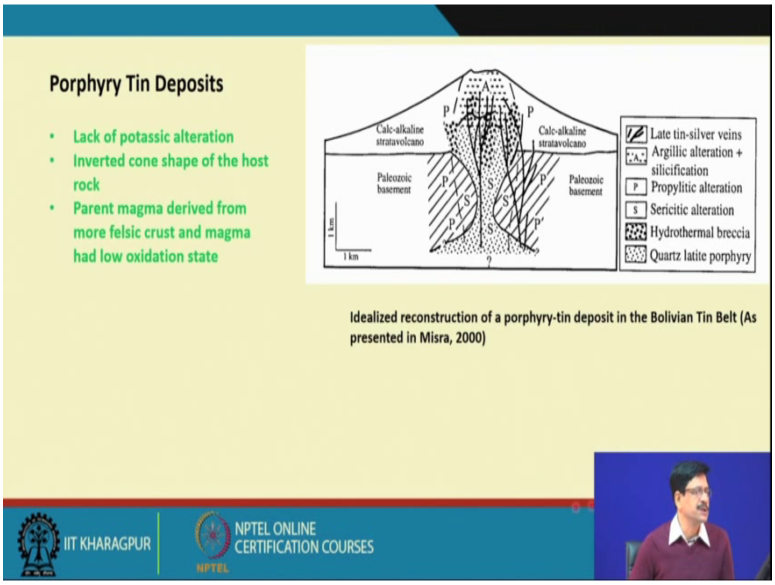

Porphyry Tin Deposits

- Lack of potassic alteration
- Inverted cone shape of the host rock
- Parent magma derived from more felsic crust and magma had low oxidation state

Idealized reconstruction of a porphyry-tin deposit in the Bolivian Tin Belt (As presented in Misra, 2000)

We do have the other class or the other type of porphyry deposit, which are the porphyry tin deposits they also do, they are mostly specially, if we look at the Chilean Mandon, Chilean Andes margin like, if this is the Chilean Andes, this generally is the, this is the porphyry copper. This is a copper belt, porphyry copper belt and a little to the east eastern side. This is the tin belt and the Bolivian tin deposits, which are observed to be occurring to the eastern or the continental side from the Andean margin. And, so, more or less confirming to the similar kind of architecture, they porphyry tin deposits. The only difference is that, the way we saw the stock, in case of the porphyry copper deposits, which is more cylindrical and is emplaced in the form of a porphyritic stock, with a small plug like body, maximum occurring within a just about a 1 square kilometre or so.

This porphyry tin deposit, the magmatic body is characteristically inverted cone shaped kind of body, and the potassic alteration zone is, zone generally misses from this porphyry tin deposits, and here, it is also observed that the or the main fundamental difference between a porphyry copper and a porphyry tin deposit is that, the parent magma, which gives rise to the porphyry tin deposits do have a much lower oxidation state, corresponding to the porphyry copper deposit. In fact, in the context of the tin and the copper deposit there is a classification scheme that was proposed for the granitoids which is basically the I type which I have already stated, which is basically the I or the I standing for igneous; protolith or igneous precursor compared to that the granitoids which are named as S type S standing for sedimentary, and these S type granites have were generated little bit away, if we look at the continental the Chilean margin.

So, here we have the Chilean Andes and the melts which are generating from here, which are more, it is coming from the melting of the slab and is basically forming the stratovolcano and that is the region for the porphyry copper deposit. The melts which are generated in these regions, if this is the Chilean Andes copper zone, then this zone actually represent the zone in which this S type magma, by melting of the already available crust, is melting to give rise to the magma which are the S type, and these S type magma are observed to be of lower oxidation state or kind of reduced maybe, because of the fact that they are derived from the sediment the melting of the sediments which are originally containing some carbonaceous material in them, because of that, the melt which is generated the s type reducing and that is how they could carry the tin in a plus 2 oxidation state, and during the later stage when had they have the fluid is mixing with fluids of higher oxidation state, the deposition is taking place.

So, the only problem, the only thing is that even though these deposits is like Bolivian tin are being labelled as porphyry type, but there are many variations in their characteristics and sometimes there are some amount of debate, as to whether they truly represent porphyry type or not, but as of the present state of their knowledge we do call them as a porphyry tin deposits.

So, thank you for today we will be continuing this discussion in the next class.

Thank you.