Mineral Resources: Geology, Exploration, Economics and Environment
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Lecture – 20
Hydrothermal Processes (Contd.)

Welcome to this lecture. We have been discussing about the hydrothermal processes and the hydrothermal deposits, we briefly looked at how to reconstruct or how to retrieve the physicochemical parameters of the hydrothermal fluid temperature, even sometimes pressure and gross chemistry in terms of the salinity; one thing is that all these divers hydrothermal mineralization environment; one thing is very common that these hydrothermal fluids, they do transport the metals in concentrations which make them deposit these metals in the form of deposits which we can which are enriched and can be worked and can be can be recovered as ores for our use.

The basic question that arises that what makes these fluid transport these metals in whatever form and we look at exactly in what form they are transported and the analysis of the present day hydrothermal fluids from the ocean floor hydrothermal systems as well as the land based geothermal systems approves or gives us conclusive evidence that these hydrothermal fluids do transport the metals in substantial quantities in concentrations to give rise to mineral deposits although it always depends on how much a what is the quantity of the fluid and what is the concentration of the of a particular metal that will vary from system to system, but the fact remains that these fluids they do transport the metals.

The question that that is posed in this context is that; what is a form in which these metals will be transported in the hydrothermal fluid.

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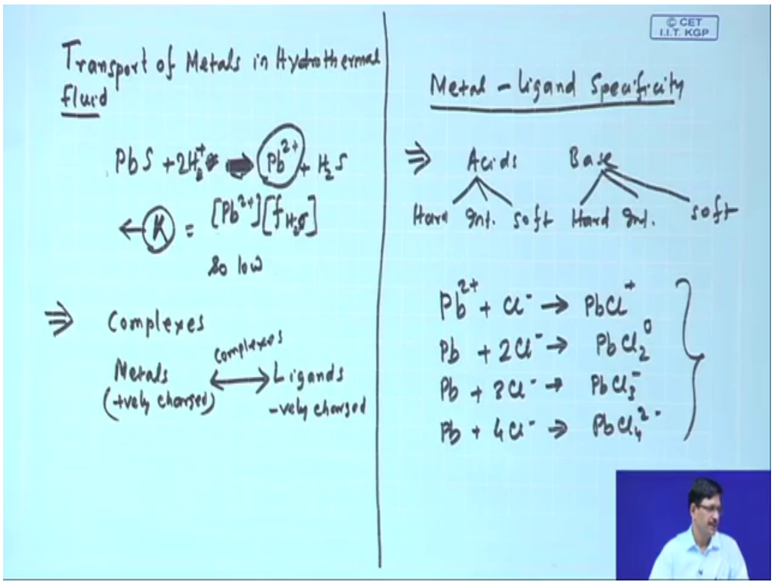

Transport of Metals in Hydrothermal fluid

$PbS + 2H_2O \rightarrow \boxed{Pb^{2+}} + H_2S$

$\leftarrow \boxed{K} = [Pb^{2+}][f_{H_2S}]$

so low

⇒ Complexes

Metals (+vely charged) $\xleftrightarrow{\text{complexes}}$ Ligands -vely charged

Metal - ligand Specificity

⇒ Acids: Hard, Int., soft; Base: Hard, Int., soft

$Pb^{2+} + Cl^- \rightarrow PbCl^+$

$Pb + 2Cl^- \rightarrow PbCl_2^0$

$Pb + 3Cl^- \rightarrow PbCl_3^-$

$Pb + 4Cl^- \rightarrow PbCl_4^{2-}$

Let us see if this; if it is possible that these metals could be transported as simple ions we can write a reaction that Pbs plus water Pb 2 plus plus H2S in such kind of a situation, we can always quantify the concentration of the metal. For example, which is led; this led its concentration will be actually be writing in terms of whatever oxygen species will come here, we can always write these the K as the led ion concentration here and the fugacity of the gas which is S 2 S over here.

So, this will come from this equilibrium constant will be a temperature dependent one and the value of this equilibrium constant will be somehow be related with led 2 plus concentration. So, if we think that this metal is being transported in the form of led 2 plus, then we have to look at what are the values of the equilibrium constant of such kind of a reaction to conclude whether such.

So, there the led will at all be transported as 2 plus ion, if so, in what concentration will be decided by this equilibrium constant value; what we observe is that this K will be so low that the it leads to very negligible concentration very very small concentration of this ion is led plus or for that matter whichever ion we consider led copper zinc or any of the metals of our interest are so low that if the metals are to be transported is metallic ions then it will not be possible to get their deposits.

So, it led people to do a lot of experiments on the hydrothermal experiments to understand the mechanism of solubility of these metals and it was observed that these metals are actually not being transported as metallic ions, but they are being transported as complexes as complexes. So, the complexes means there are metals, we can call them in the charged metallic species as the metal ions metals and they actually combine with the. So, these are generally positively charged and this is here I think in this place here, we can make a always make it a 2 H plus kind of a situation which would indicate also that it is happening in a low Ph or acidic condition which actually explains the solubility of the metals in a low Ph or acidic kind of a solution.

So, here the complexes the metals are positively charged and we say that they combine with something which is called the ligands which are negatively charged and these metals and the ligands, they combine in hydrothermal fluid to make complexes this while the metals are the metal ions the ligands could be simple or complex ions here. So, without getting into the much of the theoretical details of such kind of metal ligand complexing, we will just see whether will be we say we can rationalize or we can make some basic understanding on the transportation of the metals as metal ligand complexes and essentially the question that arises is that what makes a particular metal combine with a particular ligand to form a complex.

So; that means, or in other words that is something which will say as metal ligand specificity or a specific affinity of a particular metal to a particular ligand. So, studies on this in this particular field in this part of the solution chemistry it led us to the concept of classification of the metals and the ligands into acids and bases something similar to the Lewis acids and Lewis base.

And the acids and bases were actually divided into hard soft and intermediate hard intermediate and soft similarly the bases are also divided into hard intermediate and soft.

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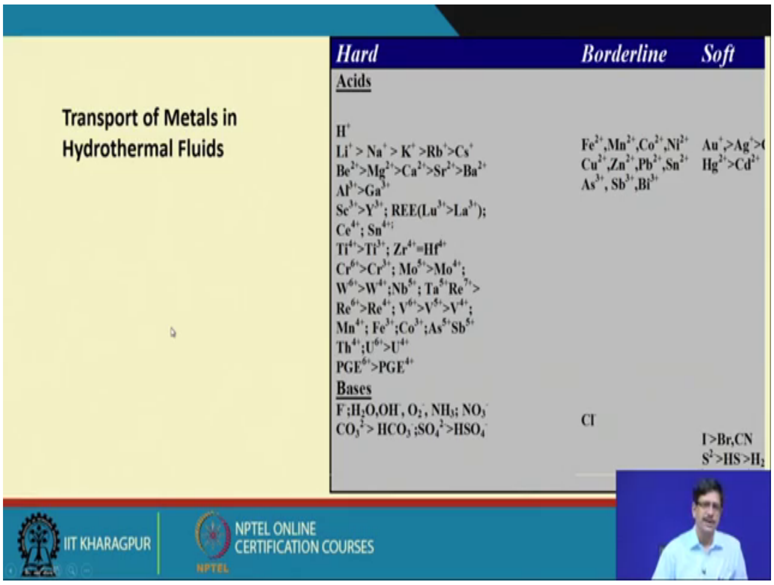

Transport of Metals in Hydrothermal Fluids

Hard	Borderline	Soft
Acids		
H^+ $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ $Al^{3+} > Ga^{3+}$ $Sc^{3+} > Y^{3+}$; REE($Lu^{3+} > La^{3+}$); Ce^{4+}; Sn^{4+}; $Ti^{4+} > Ti^{3+}$; $Zr^{4+} = Hf^{4+}$ $Cr^{6+} > Cr^{3+}$; $Mo^{5+} > Mo^{4+}$; $W^{6+} > W^{4+}$; Nb^{5+}; $Ta^{5+}Re^{7+} >$ $Re^{6+} > Re^{4+}$; $V^{6+} > V^{5+} > V^{4+}$; Mn^{4+}; Fe^{3+}; Co^{3+}; $As^{5+}Sb^{5+}$ Th^{4+}; $U^{6+} > U^{4+}$ $PGE^{6+} > PGE^{4+}$	$Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}$ $Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}$ $As^{3+}, Sb^{3+}, Bi^{3+}$	$Au^+ > Ag^+ >$ $Hg^{2+} > Cd^{2+}$
Bases		
F; H_2O, OH^-, O_2^-, NH_3; NO_3^- $CO_3^{2-} > HCO_3^-$; $SO_4^{2-} > HSO_4^-$	Cl^-	I>Br,CN $S^{2} > HS > H_2$

This figure here gives this table which is shown in the this table shows a classification of the metals; metals and the ligands into hard borderline and soft intermediate is essentially borderline. So, which are the hard acids the hard acids are the ones which have the high charge where radius ratio there will be monovalent alkaline elements like the lithium sodium potassium or the high field strength element like scandium yttrium tungsten; tungsten 6 plus tungsten 4 plus you could see a tungsten 6 plus with a higher charge has a higher charge by radius and that is why is a much harder received, then even tungsten 4 plus.

So, most of the metals of our interest manganese iron 3 plus cobalt 3 plus arsenic, these metals essentially having a very high charge by radius ratio are classified is titanium zirconium hafnium molybdenum antimony platinum group of elements uranium 6 plus uranium 4 plus these are all coming under the category of hard acids the borderline acids are ion so; obviously, those which are the bivalent ones like iron 2 plus manganese cobalt nickel copper 2 plus zinc 2 plus led 2 plus tin arsenic 3 plus these are coming under the category of the borderline metals on the basis of their charge by radius ratio and metals like gold silver mercury cadmium these are coming on the soft category of acids.

Similarly, the bases fluoride hydroxide oxide bi sulfate and sulfate where they are the complex anions it is not an exhaustive list of the anions and cations, there could be there are other ligand such as organic ligands also could be incorporated here according to there, but then we are seeing the most common ones and we see the chloride which is the which with the most soluble or the of these species in hydrothermal fluid or the occurring in maximum concentration in almost all types of hydrothermal fluids is coming under the borderline category and bi sulfide sulfide H2S cyanide bromide kind of cations are coming anions are coming in the class of soft acids.

What does it tell us without getting into much of the theoretical details it gives us a broad framework to understand that hard acids are likely to combine with hard bases to form there complexes borderline acids will combine with the borderline ligand to form their complexes that is how we could correlate that led 2 plus zinc 2 plus copper they will form the chloride complexes and soft metals like gold silver mercury will readily form there bi sulfides sulfide kind of complexes.

So, this gives us a very broad outline although the exact mode in which the metal is transported depends on which of these species are more dominant and there is always a competition for the metals to be combining combine with the particular say for example, experiments and these also are very much dependent on the stability of such kind of ligands. For example, the sulfurous species will be very much a strong dependent on the PH.

So, depending on the Ph of the environment if it there is the dominance of the bi sulfide or the sulfide species then only the gold or the silver or the mercury will get the opportunity to get complex as bi sulfide; sulfide otherwise if there is a dominance in the chloride and also these kind of complexes are an a function of the dominance of the type of complex which forms a function of the temperature and, but within those limitations these give us a good guideline to understand which of the metals are being transported in what form.

So, it helps us also to subsequently when the during the deposition process what kind of physicochemical change we would expect for the metals to be deposited because this mineralization process involves the substantial solubility of these metals in the hydrothermal fluid under a given physicochemical condition and we require we need to have a change to be brought about in the environment the chemical environment. So, that the metals will deposit to will deposited in the metals the solubility will decrease and there will be deposited as their respective minerals.

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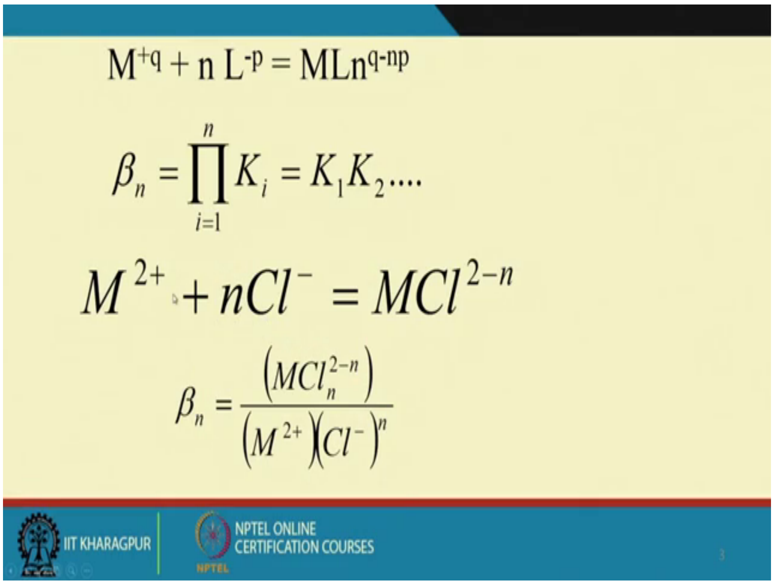

$$M^{+q} + n\,L^{-p} = MLn^{q-np}$$

$$\beta_n = \prod_{i=1}^{n} K_i = K_1 K_2 \ldots.$$

$$M^{2+} + nCl^{-} = MCl^{2-n}$$

$$\beta_n = \frac{\left(MCl_n^{2-n}\right)}{\left(M^{2+}\right)\left(Cl^{-}\right)^n}$$

So, here we can represent this is the metal ion. So, the complex can be represented if it dominantly happens to be chloride complexing because the chloride complexing is the one which has been very extensively studied through experiments. So, this gives a schematic relation the metal ion with q plus charge and the number n number of the ligand with minus p charge will form a complex which is MLn q minus np.

So, either it will be a being a positive charge or the negative charge will depending on the value of n and here we can represent the equilibrium constants and formation constants of such kind of complexes through generally represented equilibrium constant as beta n which will be K 1, K 2, K 3 or K 4 which I will be just explaining the next slide.

So, here the concentration here is this, this the combination is that M suppose the bivalent metal with 2 plus charge and n number of chloride and forms a metal chloride complex then this will be forming a complex which will be MCl 2 minus n and the equilibrium constant is expressed as the concentration or the activity of the mc this complex which has got a charge of 2 minus n and this is how the concentration can be expressed.

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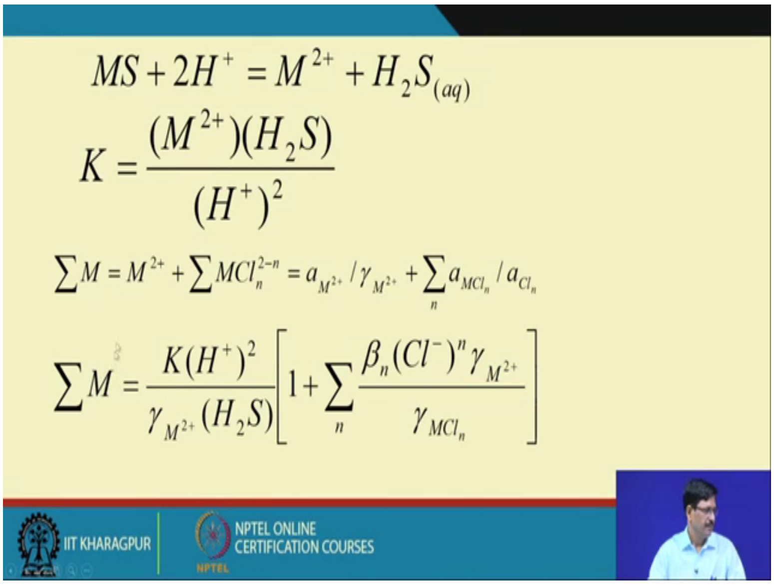

$$MS + 2H^{+} = M^{2+} + H_2S_{(aq)}$$

$$K = \frac{(M^{2+})(H_2S)}{(H^{+})^2}$$

$$\sum M = M^{2+} + \sum MCl_n^{2-n} = a_{M^{2+}} / \gamma_{M^{2+}} + \sum_n a_{MCl_n} / a_{Cl_n}$$

$$\sum M = \frac{K(H^{+})^2}{\gamma_{M^{2+}}(H_2S)}\left[1 + \sum_n \frac{\beta_n (Cl^{-})^n \gamma_{M^{2+}}}{\gamma_{MCl_n}}\right]$$

So, here if we take a sulfide like just we just reaction that I wrote for a sulfide like galena which is MS plus 2H plus is giving rise to a bivalent and M 2 plus and H2S aqueous. So, here the equilibrium constant is given by this expression which is M 2 plus into these. So, here these are essentially representing the terms which are the thermodynamic concentration or the activity and in case, it is a; it happens to be a gaseous species, we can represent it as fugacity or the corrected partial pressure and if we take ideal conditions then they all be representing a simple concentration terms for example, for a metal it will be representing a term concentration term as molal or in case of a species like H2S, we can always represent it in terms of atmosphere.

And now if we try to find out the what exactly is the total amount of the metal M which is there in the solution then we have to consider the metal to be present in the form of M 2 plus and the total concentration of the all the metals which is complexed in difference stoichiometry because this is summation term so; that means, if happens to be a MCl or MCl 2 or MCl 3 and so on, then the total concentration will be coming out of all the complexes possible complex stoichiometry responsible for a bivalent metal like say for example, led.

So, here for the time being, even you can ignore this activity coefficient term because we have and we are taking them to be ideal and activity coefficient take them as one. So, this becomes this the total solubility become the activity of the metal ion plus all the activities of the chloride ion or in terms of their concentration now here we can replace since since the equilibrium constant through this reaction is coming out in the form of the H2S gas partial pressure here we can replace M 2 plus from this equation as the equilibrium constant into the hydrogen ion concentration square divided by the fugacity of H2S and these keeps as an expression.

So, this is a total concentration of the metal. So, as we stated before that if we consider the metal to be transported only as metallic 2 plus ion and the because of the equilibrium constant very low equilibrium constant of this kind of reactions, but in actual what is happening is that this metal like M with availability of the ligand which is chloride is able to form complexes and the total solubility of the metal is contributed by formation of the complexes of the metal.

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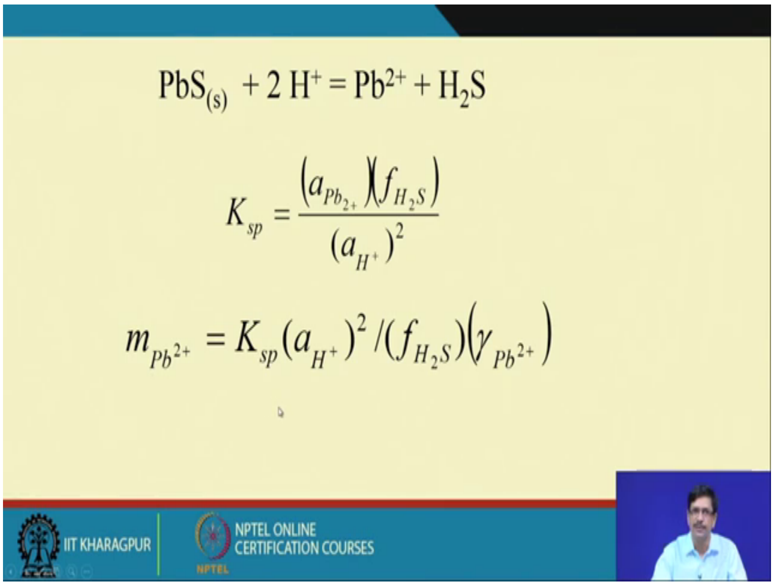

$$PbS_{(s)} + 2\,H^{+} = Pb^{2+} + H_2S$$

$$K_{sp} = \frac{(a_{Pb_{2+}})(f_{H_2S})}{(a_{H^{+}})^{2}}$$

$$m_{Pb^{2+}} = K_{sp}(a_{H^{+}})^{2}/(f_{H_2S})(\gamma_{Pb^{2+}})$$

Here is the example that take a metal like led. So, here this is the solubility product which is activity of the concentration of the led 2 plus and the fugacity of H2S by the activity of hydrogen ion square and the total concentration of the led expressed is molal is given by an expression where it is the solubility product of this reaction into the Ph divided by the fugacity of the partial pressure of H2S.

So, what is coming out from here it gives us a clear cut idea that the solubility of the metal is dependent on one of the important parameters that comes here is the ph. So, the Ph has to be has to have the value which will are directly. So, when the activity of H plus ion will be directly responsible to what the concentration of the total metal is and other variables are also contributing to it.

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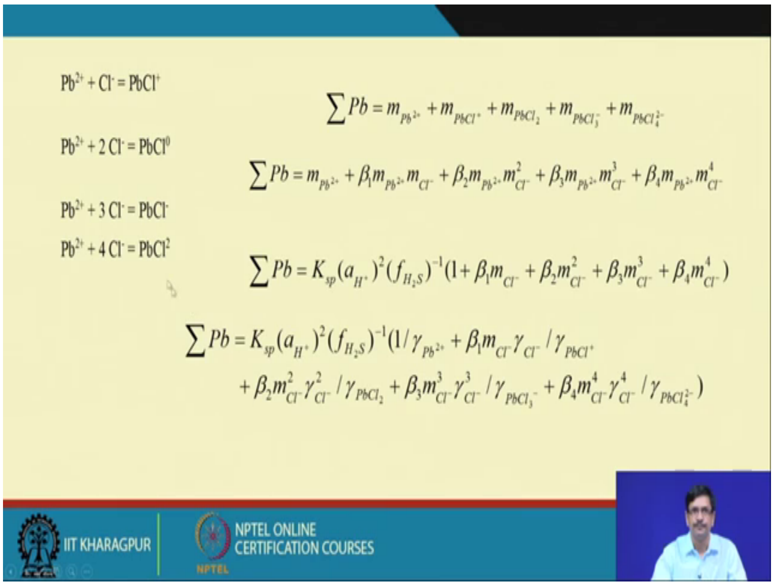

$Pb^{2+} + Cl^{-} = PbCl^{+}$

$Pb^{2+} + 2\,Cl^{-} = PbCl^{0}$

$Pb^{2+} + 3\,Cl^{-} = PbCl^{-}$

$Pb^{2+} + 4\,Cl^{-} = PbCl^{2}$

$$\sum Pb = m_{Pb^{2+}} + m_{PbCl^{+}} + m_{PbCl_2} + m_{PbCl_3^{-}} + m_{PbCl_4^{2-}}$$

$$\sum Pb = m_{Pb^{2+}} + \beta_1 m_{Pb^{2+}} m_{Cl^{-}} + \beta_2 m_{Pb^{2+}} m_{Cl^{-}}^{2} + \beta_3 m_{Pb^{2+}} m_{Cl^{-}}^{3} + \beta_4 m_{Pb^{2+}} m_{Cl^{-}}^{4}$$

$$\sum Pb = K_{sp}(a_{H^{+}})^{2}(f_{H_2S})^{-1}(1 + \beta_1 m_{Cl^{-}} + \beta_2 m_{Cl^{-}}^{2} + \beta_3 m_{Cl^{-}}^{3} + \beta_4 m_{Cl^{-}}^{4})$$

$$\sum Pb = K_{sp}(a_{H^{+}})^{2}(f_{H_2S})^{-1}(1/\gamma_{Pb^{2+}} + \beta_1 m_{Cl^{-}}\gamma_{Cl^{-}}/\gamma_{PbCl^{+}} + \beta_2 m_{Cl^{-}}^{2}\gamma_{Cl^{-}}^{2}/\gamma_{PbCl_2} + \beta_3 m_{Cl^{-}}^{3}\gamma_{Cl^{-}}^{3}/\gamma_{PbCl_3^{-}} + \beta_4 m_{Cl^{-}}^{4}\gamma_{Cl^{-}}^{4}/\gamma_{PbCl_4^{2-}})$$

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Now, coming to the actual mechanism taking the example of led here. So, if we consider that led is a bivalent metal and the in a hydrothermal fluid we have we have we have abundant chloride ion as the complex as the as the ligand, then led can possibly form a series of such complexes as a led Cl whole plus led Cl led Cl 2 this is actually this is PbCl 2 there is a mistake there. So, Pb; Pb 2 plus plus 2 Cl minus this will be PbCl 2 0 and in this case. So, I just correct it correctly write it out here PbCl plus led plus 2 Cl minus PbCl 2 0 led plus 3 Cl minus PbCl 3 minus and led plus 4 Cl minus PbCl 4 2 minus. So, these are these are the correct species which form as the complexes are for led. So, if you could see on this.

So, then here the total concentration of led here is being shown as the total concentration is coming from the molality the concentration of led in the form of led 2 plus led led Cl plus let Cl 2 0 led Cl 3 minus and led Cl 4 plus now this can be expanded in the form because for each of these complexes led Cl plus led Cl 2 0 and led Cl 3 minus and led Cl 4 2 minus 3 2 minus we will have can be relate they can be related to the concentration of the total chloride MCl in terms of molality of chloride with the form with the formation constant like K 1 which is for the formation of this led Cl K 2 or represented as in general term is beta 1; so, beta 1, beta 2, beta 3 and beta 4 with the concentration of the ligand which is your chloride over here.

Now, we can make out from here and again we will replace the molality; term molality for led plus as a solubility product of the reaction which is led sulfide plus h plus giving rise to led ion and H2S. So, here will be replacing the H2S term here. So, the total solubility of led in the hydrothermal fluid will be contributed by these many factors out of which something which is coming out to be very very prominent is that the concentration of the chloride ion.

So, the amount of the metal taking example for a metal like led here in this situation would be similar for other bivalent metals like zinc is also that the solubility the total the total capacity or the capability of that particular fluid to transport led soluble form to give rise to a mineral deposit finally, when it gets deposited is depending largely on the concentration of the chloride ligand.

So, even if we this is only expanded in the form of the activity coefficient which can which are all taken as one. So, if you take the activity coefficients in this equation all as one it will be reduced to this equation only ok.

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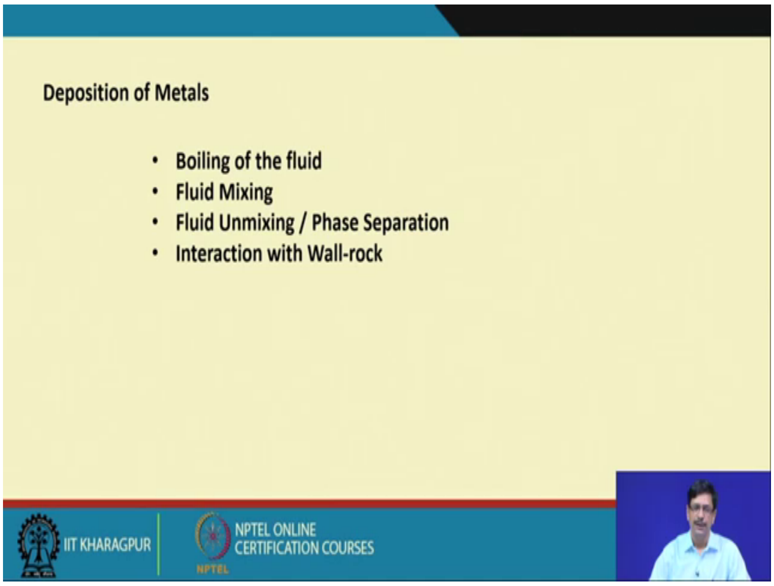

Deposition of Metals

- Boiling of the fluid
- Fluid Mixing
- Fluid Unmixing / Phase Separation
- Interaction with Wall-rock

So, likewise there have been several experimental study on the solubility behavior of gold as different complexes as chloride and bi sulfide solubility of many of these base metals copper led zinc in hydrothermal fluids in different wide range of temperature and a composition mainly affected by the ph.

So, there is some there is a good amount of knowledge and better and the information that is available to us that under divers type of ore forming environments hydrothermal environments that we have discussed the metals are dominantly transported in the form of metal complexes likes chloride complex is one as dominant metal that could be bicarbonate complex thing that could be bi sulfide sulfate and other type of complexing depending on the gross chemistry of the fluid.

So, in order to get the hydrothermal fluid deposit in the form of a mineral deposit are in whole body we need to have to we need to have a change in the physicochemical environment changing change over from a dominantly from a transport transporting resign to a depositional resign . So, this is brought about is we have already discussed before in the context of fluid inclusion that the basically brought about by processes boiling of the fluid mixing up the fluid; fluid unmixing or phase separation and interaction with the wall rock.

So, these may be that they operate in combination and then as we stated in the very beginning while regarding the ore deposits the these process have to operate at a particular scale and then in an optimum intensity and in optimum environment which will give rise to a hydrothermal deposit; deposit of a of a size in terms of it is the quantity of the metal that will be deposited in a particular locale to give rise to a deposit sometimes they do give rise to deposits which are fairly large in size giving a good amount of the metal in terms of the total tonnage that is available and sometimes the situation if the conditions are not that very favorable they result in what we call as a lien or not. So, reach mineral deposits.

So, then if we want; so, now, once we are going from a transporting to the depositional resign then we see the what exactly we would expect.

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Consequences of Metal Deposition

HYDROTHERMAL ALTERATION

- Porphyry-type Deposits (Cu, Mo, Au)
- Skarn Deposits (Sn, W sometimes Au, Fe, Mo)
- VMS (Cu-Pb-Zn)
- Lode-type Gold Deposits
- Epithermal Deposits

NOMENCLATURE VIS-A-V-S MINERALOGY

- Potassic : Mostly as a result of addition of K with K-feldspar and biotite as the dominant minerals. Plagioclase feldspar is usually replaced by K-feldspar and amphibole by biotite
- Phyllic : Hydrolysis of wall rock minerals - Sericite forms at the expense of K-feldspar; sercite and quartz are the dominant minerals
- Argillic: Further hydrolysis of K-mica (sercite) and formation of kaolinite at the expense of K-mica
- Propylitic: Epidote, chlorite with or without calcite
- Advanced Argillic: Typically contains alunite ($KAl_3(SO_4)_2(OH)_6$) and represents very low pH

For example; so, the hydrothermal mineralization as a whole; on a whole when whenever they fluid is transporting the metal where the temperature may it could be because if it is temperature dependent temperature is higher, if its pressure has got because we will see the role of pressure again sometime in the course of the lecture the oxidation state if it happens to be a more near surface if the Ph; Ph conditions and so on and then when the deposition is taking place in any local here we would expect a gross difference in the chemistry of the I mean the fluid and the country rock will be in gross disequilibrium with each other.

So, they would also they fluid when its depositing the metal we leave its imprint in some form which we broadly categorized as the hydrothermal alteration which will be discussing in detail in the next class first just to give you an idea.

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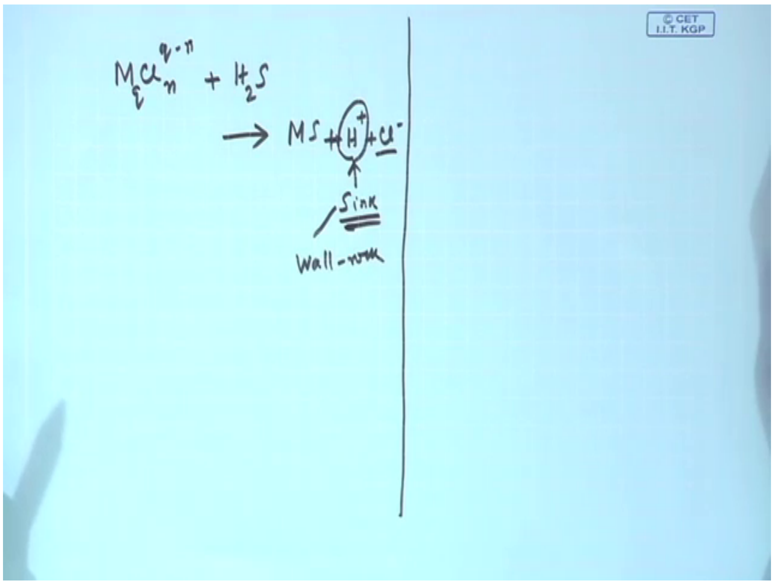

$$MCl_n^{q-n} + H_2S \rightarrow MS + \boxed{H^+} + \underline{Cl^-}$$

For example in a metal which is being complexed as MCln q minus n kind of a complex and that is now coming in contact with or that is now coming to a situation where there is the partial pressure of H2S as increased to the extent even though I am not writing any balanced equation here I will simply just put it as MS if this particular complex of a metal chloride is getting sulfidized to give rise to the metal sulfide as MS then it is definitely going to liberate this species in the solution.

So, as a as a direct consequence of the position of this metal complex to a sulfide there will be release of this H plus in the in the fluid; so, in order for the particular reaction to advance or to go on to completion, there must be something which will absorb this h plus or which will act as a sink for this h plus to be accommodated. So, that possibly is only will be done by the wall rock and in this process the hydrothermal this whole spectrum of hydrothermal mineral deposits that we have listed out in the beginning the magnetic metamorphic the surface operatory volcanogenic volcan associate epithermal deposits or the volcanogenic acid sulfide deposit in operating in the seafloor mid oceanic these systems all these systems are very characteristically associated with something which we call is hydrothermal alteration if we see it here.

So, the consequences immediate consequence of the mineralize and hydrothermal mineralization process results in something called hydrothermal alteration. So, these hydrothermal alteration the nature of the hydrothermal alteration the exact mismatch in the chemistry of the wall rock and the hydrothermal fluid and what exactly happening in terms of formation of the secondary minerals in the wall rock as hydrothermal alteration zone whether there will be occurring as a single zone or multiple sub such zones are arranged in arranged in space.

We will look at them individually when we look at these deposits, but these hydrothermal alteration zones are very very prominent in deposits like porphyry of deposit skarn deposits a vms the lode type deposit the epithermal deposits and we there are some nomenclature which are proposed for such kind of hydrothermal deposits like potassic alteration phyllic alterations argillic alterations propylitic alteration advanced argillic alteration these alterations are all terminologies associated with the arphilic of a deposits in the in the convergent plate boundaries like the onion margin.

So, potassic alteration is one which takes place when the Ph of the fluid is rather high and it is in the potassic stability field temperature is high and it is the original magnetic fluid at high temperature and gradually when the temperature is decreasing and the fluid is interacting with other fluids are like a metallic fluid source, then it is giving rise to alterations zones is a dominated by minerals which is sericite or sometimes even the and also it does indicate that the alteration alteration zones are developing as if as a function of the increasing water by rock ratio and we will look at the details of the and there are many other types of alterations which take place in many different deposits like this characterized by a very typical alteration there are sometimes addition of silica in the form of silicification.

So, addition of carbon dioxide formation of the carbonate led carbonate type of alteration and we will look at them and so, in summing up for this, but this week’s course that we look at the sources of hydrothermal fluids possible different possible sources their gross chemical and thermal characteristics how to retrieve the information on the physicochemical parameters by study by studying the mineralogy by studying the fluid inclusions in them and got a got a brief idea about the mechanism of transportation of the metals in hydro thermal fluid and deposition and we will see the individual types the different types of alteration zones which are associated with these deposits in the subsequent discussions.

Thank you.