Mineral Resources: Geology, Exploration, Economics and Environment

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Lecture – 18
Hydrothermal Processes (Contd.)

Welcome to the lecture we were discussing about the and about a method which we adopt to retrieve temperature of formation temperature of the hydrothermal fluid that give rise to mineral deposits. We have already defined them fluid inclusions are tiny fluid filled cavities inside the host mineral; a mineral in which they occur, we call them as host mineral and they are trapped during the primary growth of these minerals from the fluid and in they do also form within the minerals at any time later after their formation on of healed cracks heal fractures within the minerals and we defined them that.

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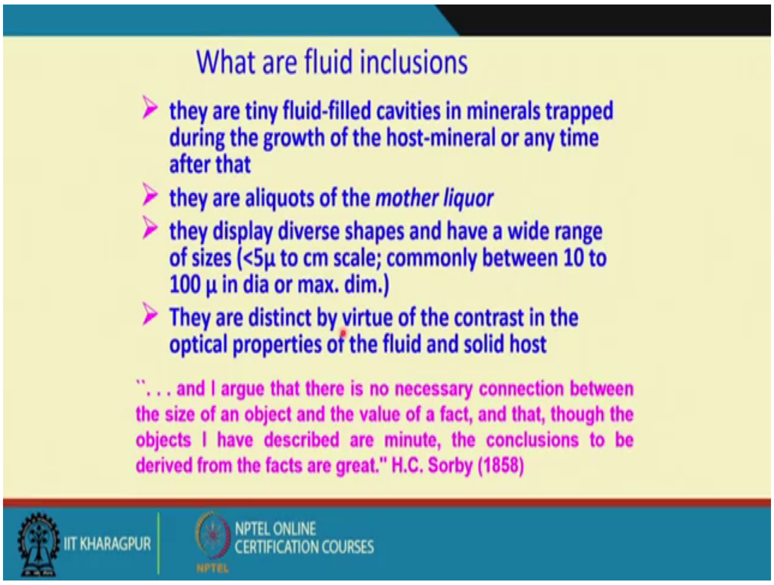

What are fluid inclusions

- they are tiny fluid-filled cavities in minerals trapped during the growth of the host-mineral or any time after that
- they are aliquots of the *mother liquor*
- they display diverse shapes and have a wide range of sizes (<5μ to cm scale; commonly between 10 to 100 μ in dia or max. dim.)
- They are distinct by virtue of the contrast in the optical properties of the fluid and solid host

"... and I argue that there is no necessary connection between the size of an object and the value of a fact, and that, though the objects I have described are minute, the conclusions to be derived from the facts are great." H.C. Sorby (1858)

They are fluid filled cavities, they are the aliquots of the mother liquor just to recapitulate.

They display diverse shapes and sizes and they do have a very good contrast optical contrast with the host mineral in which they occur.

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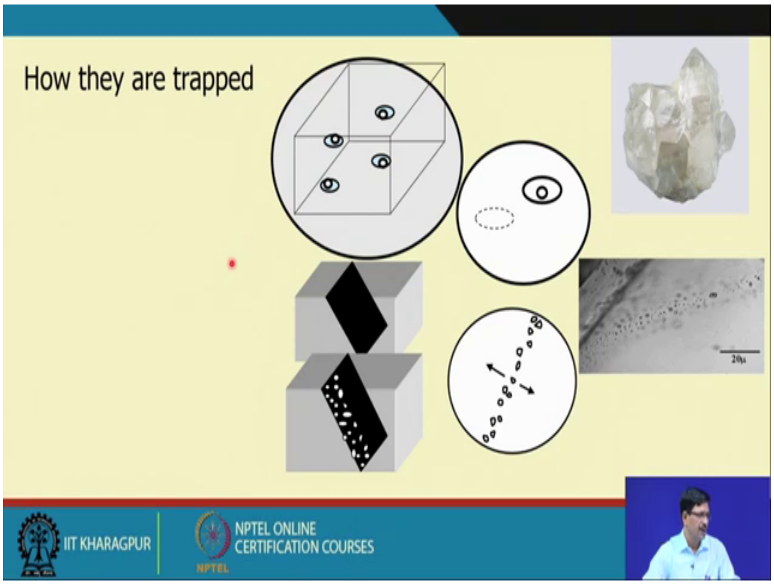

How they are trapped

And just to; just for a recapitulation, this diagram represents the process in which the primary. So, we name; we or we call these inclusions which are the part of the random three dimensional network as the primary inclusions the primary inclusions and we when we take a section and study under the microscope, we see these different inclusions getting focused at different planes compared to the minerals which the fluid inclusions which are aligned on linear arrays essentially the sections of the inclined fracture plane as it is shown here.

And they are generally if they are traverse across many such grains of this host mineral, then we call them with the secondary inclusions. Since we talk about the fluid from which the minerals precipitate, we will generally be focusing on the characteristics of these primary fluid inclusions, but sometimes the hydrothermal fluid activity take place in a manner in the protracted manner in episodic growth of the hydrothermal vein like one like the one which is shown here which makes even if we can establish a continuum of the fluid activity in different phases in giving rise to mineralizations in different generations.

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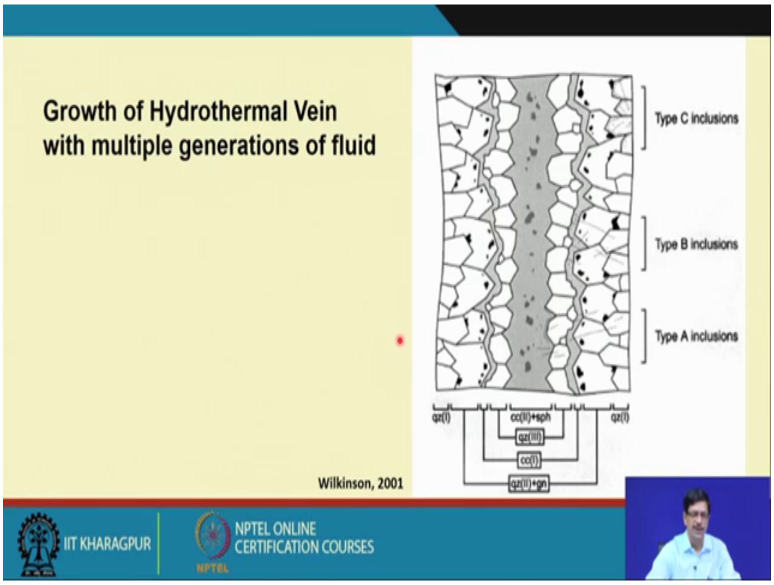

Growth of Hydrothermal Vein with multiple generations of fluid

Wilkinson, 2001

Then the inclusions which occur a secondary inclusions in the older phases host grains would also give useful information to us in this diagram we can see that this; this is a typical example of the formation of hydrothermal veins in the normal crustal rocks in response to fractures their fractured filling.

So, on these we see that the first generation of quartz were deposited on the fracture wall then there was a second phase of fracturing and fluid flow and in which the second generation quartz precipitated from a fluid and that fluid could eventually be trapped a secondary inclusions in the earlier generation quartz and so on. So, this diagram which has been taken from Wilkinson 2001 from one of the research papers on hydrothermal deposits.

So, this gives us a very clear idea as to the fluid the fluid deposition process formation of the hydrothermal veins in different generations and the importance of the hydrothermal the importance of the study of the fluid inclusions sometimes it may so happen, but if the fluid activity takes place with a very substantial time gap and with no relationship to the earlier stages of fluid activity in that cases the secondary fluid inclusions will not of much use to us well.

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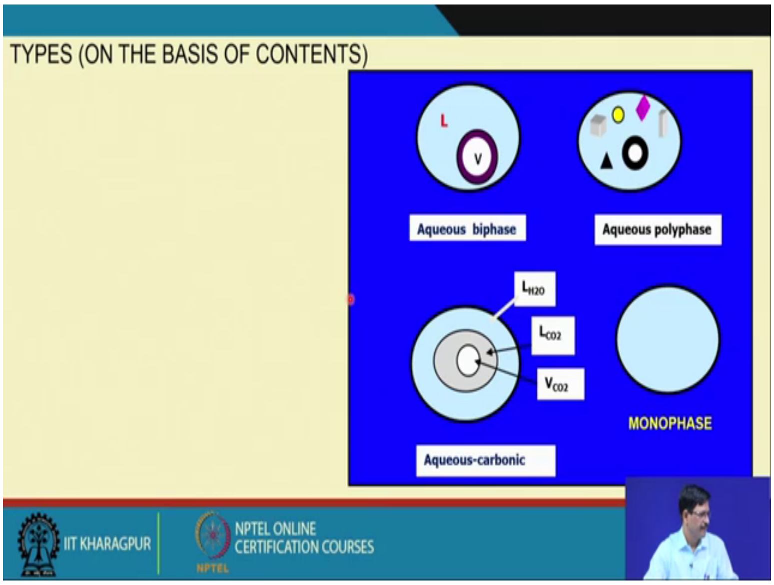

TYPES (ON THE BASIS OF CONTENTS)

So, getting into the fluid inclusion types here its shown on the diagram; it is the case where it is a liquid plus vapor aqueous inclusion aqueous liquid and aqueous vapor which we can identify under the microscope from their optical properties and this is a sketch of an aqueous inclusion which may occur with number of such mineral phases which are called as the daughter phases we can see here like a halite sodium chloride. This is potassium chloride. This is a calcium carbonate calcite. This is anhydride, even this can also happen a sulfide a chalcopyrite small grain of chalcopyrite also within the within the inclusion cavity.

This represents the wall of the inclusion which is essentially behaving as a closed system this is just a case that in the compared to a situation here where the fluid could be visualized as having very little concentration of the other dissolved species as against that this inclusion represents a fluid which was originally very very briny or very concentrated in many digital solids and which gave rise to the this kind of a mineral phases precipitating out in the inclusion cavity after the entrapment of this particular fluid this is an example of a situation where an aqueous liquid and a carbonic liquid are present indicating that this must be a situation where the fluid had appreciable concentration of carbon dioxide which will be discussing.

They may also occur is mono phase conditions only a liquid or a vapor.

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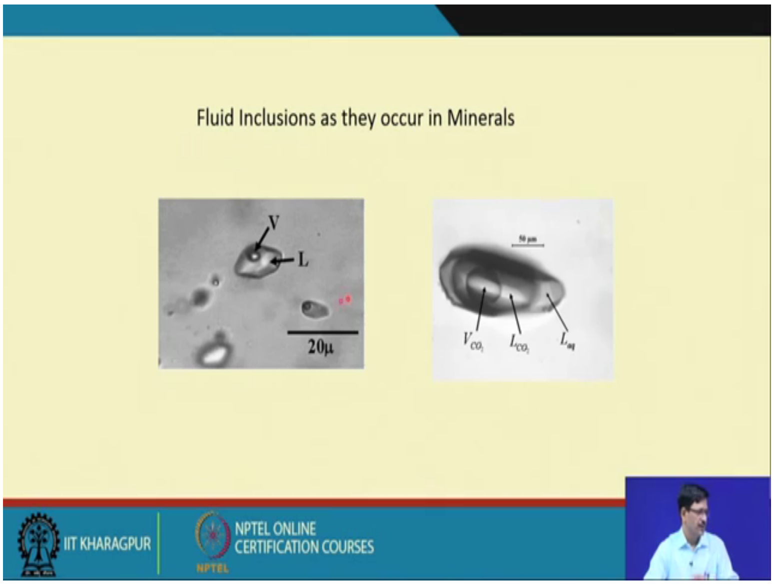

Fluid Inclusions as they occur in Minerals

So, here are some real; a some photographs from fluid inclusions as they are observed in host minerals this is an example of aqueous y phase inclusion where the a vapor and the liquid are labeled as v and l and you could see from the micron bar which is 20 micron that you can imagine; what could be the maximum dimension of this and what I mean by having it optical contrast with the host grain you could see a very clearly demarcated boundary or the wall inclusion wall within which the inclusion is present and this is an example of a mixed inclusion where it is a; what liquid water the liquid carbon dioxide and carbon dioxide vapor the significance of these inclusions will be discussed in the course of this discussion.

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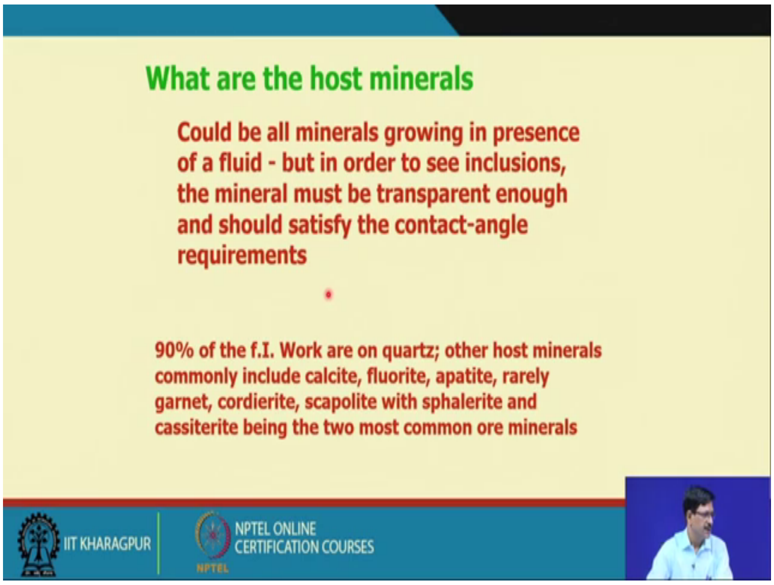

What are the host minerals

Could be all minerals growing in presence of a fluid - but in order to see inclusions, the mineral must be transparent enough and should satisfy the contact-angle requirements

90% of the f.I. Work are on quartz; other host minerals commonly include calcite, fluorite, apatite, rarely garnet, cordierite, scapolite with sphalerite and cassiterite being the two most common ore minerals

So, then let us see; what are the host minerals in which we see the minerals. In fact, any mineral that is crystallizing from a fluid is likely to trap the inclusion only it is our capability to see the inclusions under the microscope in which kind of light because we know, there are sulphide minerals or oxide minerals ore minerals which are opaque to a normal visible range of the light whereas, the silicate minerals like quartz or carbonate like calcite or fluorite apatite kind of gangue minerals, sometimes, they are even observable in many other gang minerals, but the majority of the fluid inclusion work is actually on quartz which is a ubiquitous host in many of the ore deposits in oxide and sulfide deposits as we see them.

So, 90 percent of the fluid inclusion works around quartz other host minerals are calcite fluorite apatite rarely garnet cordierite scapolite and so on.

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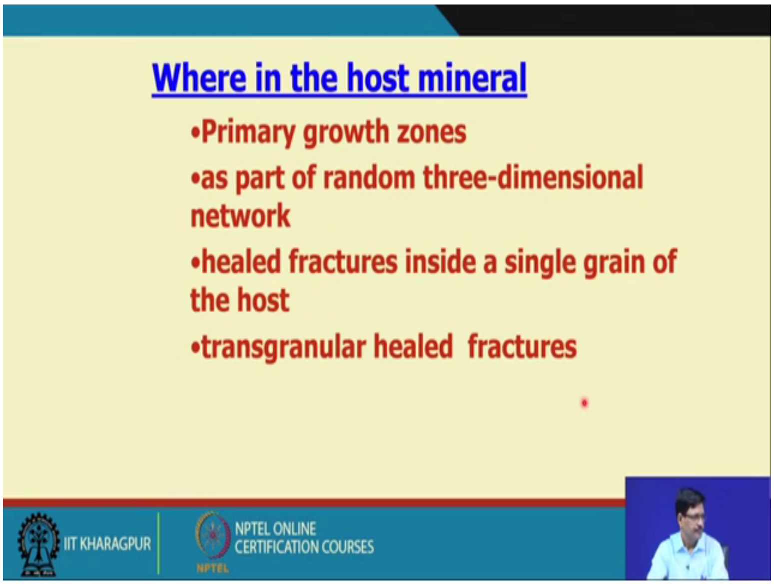

Where in the host mineral

- Primary growth zones
- as part of random three-dimensional network
- healed fractures inside a single grain of the host
- transgranular healed fractures

So, as I discuss; as I pointed out that these fluid inclusions could be in primary growth zones could be as part of the random three dimensional network as I shown in the diagram they could be on the healed fractures inside the single grain of the host or these kind of fractures could be transgressing through many grains when the when the fracturing has taken place after the formation of the hydrothermal vein or the ore body they are the transgranular healed fractures.

So, in these cases, when the minerals are present in primary growth zones or in part of the random three dimensional network we call them as primary inclusions and when they are present on a linear arrays on the healed a cracks or fractures traversing through many grains within the host minerals, we call them in the secondary inclusions.

This is general terminology which we follow in fluid inclusion literature as primary and secondary although it becomes sometimes not a very easy task to distinguish them and the healed fractures inside a single grain of the host sometimes is we use a word; a pseudo secondary is essentially, it represents the fracture which is within the single grain of the host mineral which is not a transgress through many through the entire about entire body of these quartz vein of the ore body.

There, we use the word as pseudo secondary otherwise the broad classification of the inclusions to primary and secondary is having a connotation of time that the primary inclusions which form during the growth or during the formation of the host mineral and the secondary inclusions formed anytime afterwards.

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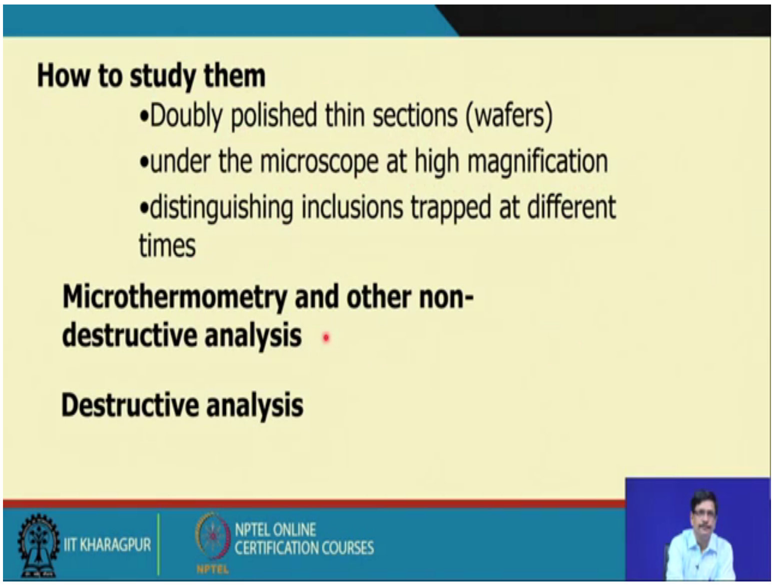

How to study them

- Doubly polished thin sections (wafers)
- under the microscope at high magnification
- distinguishing inclusions trapped at different times

Microthermometry and other non-destructive analysis

Destructive analysis

So, we study them in the laboratory by using doubly polished thin sections of a certain thickness because these inclusions are several tens of microns in dimension.

So, the thickness of the sections should be should be at least 4-5 times the maximum dimension expected. So, generally they are 200 to 300 micron in thickness. We study them under the microscope at high magnification and then we do an experiment which is essentially we call as micro thermometry and other non destructive analysis or sometimes we can do some destructive analysis by opening the inclusions or taking the sample taking the inclusion fluid out of the host mineral and analyzing them using many sophisticated analytical equipment.

We will be discussing about the micro thermometric technique which is the which is the which provides the most fundamental and the first level information of these fluid inclusions.

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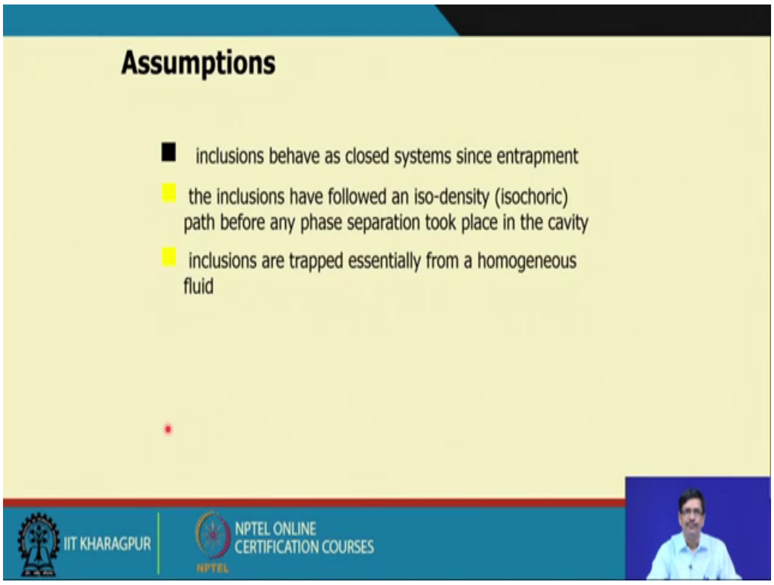

Assumptions

- inclusions behave as closed systems since entrapment
- the inclusions have followed an iso-density (isochoric) path before any phase separation took place in the cavity
- inclusions are trapped essentially from a homogeneous fluid

So, we before we look into the fluid inclusion exercise and the data that we retrieve from them we lets first see that the assumptions that we make before we proceed on to study the fluid inclusions that the inclusions behave is closed system since the entrapment there is no loss or gain of any component with the surrounding in the within the host mineral.

And the inclusions behave as a closed system and have followed a constant density constant volume constant composition path which we call as the isochore and inclusions are trapped essentially from a homogenous fluid and the entrapment; entrapment process is essentially homogeneous.

So, the figures that I showed you here this figure essentially whatever is where we are seeing them as heterogeneous assemblies, but these all are the post entrapment phase changes that we see in these inclusions rather than the inclusion being trapped in this condition the entrapment is essentially homogeneous and a fluid the entrapment is from a homogeneous fluid and also the entrapment process is homogeneous.

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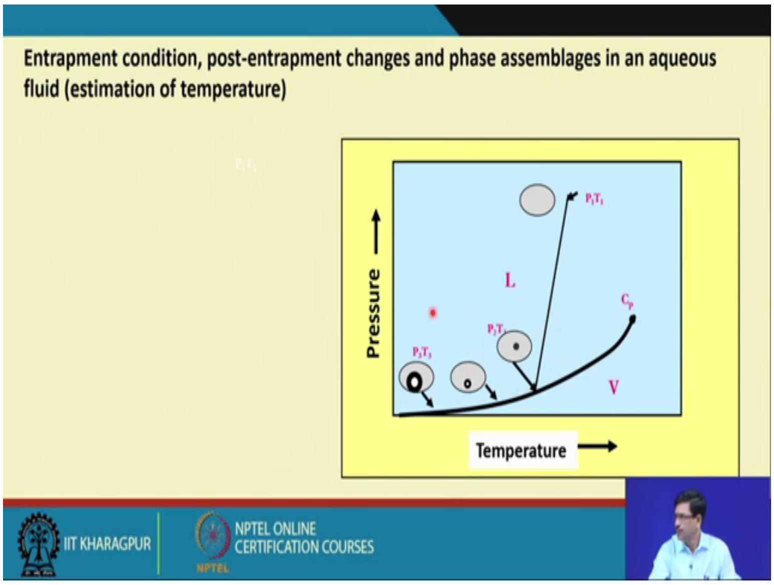

Entrapment condition, post-entrapment changes and phase assemblages in an aqueous fluid (estimation of temperature)

We will be able to explain the formation of these fluid inclusions in a very simple manner here what I could see here. So, this is a unary phase diagram of water here is the critical point corresponding to 374 degree centigrade and 220 bar. So, this is the vapor stability field this is the wok this is the liquid water stability field.

Let us assume that there is a temperature and pressure conditions to P 1 and T 1, where this mineral precipitated from a fluid on a fracture or any rock that is in the subsurface and when this mineral is once it is trapped it is behaving as a constant density constant composition on a system, we do not any exchange of component with a host mineral and then the condition at which we are seeing them in the laboratory is different from the condition where it was entrapped.

And since the path that it follows is an isochoric path; that means, a constant slope dp by dt path. So, it follows a straight line path with the decrease in pressure and temperature conditions with larger dig in larger decrease in pressure with smaller d in decrease in temperature and it evolves in the same one phase condition without undergoing any phase change till the till they till it reaches a point here which corresponds to the boiling curve of pure water.

So, here the liquid and vapor; so, this curve corresponds to the liquid vapor coexistence or which we call as the boiling curve and as in when it intersects the point here a vapor small vapor bubble nucleates from this within this week inclusion cavity.

This can be explained on the basis of the differential contraction of the host mineral and the liquid because liquid has got a higher coefficient of thermal expansion than the host solid or it could also be explained on the base purely on the basis of this phase diagram that is it not when it intersects the point here one vapor gets the vapor bubble gets nucleated and comes into existence.

So, from a homogenous entrapped condition now it attains a heterogeneous state with the liquid plus vapor any further decrease in the pressure and temperature will make it move on this boiling curve because it cannot leave the boiling curve as long as the vapor and liquid are coexisting and with further decrease in the pressure and temperature will only result in an enlargement of this originally trapped tiny bubble till the point it reaches here corresponding to the room temperature where we are observing it.

Where we see that this inclusion is the way we see is a vapor and a liquid. So, this is how we can we can explain the entrapment process of fluids during the mineralization process and assuming that the host mineral which was precipitating here was also precipitating along with our ore minerals and that represents the thermal characteristics as well as the some chemical characteristics of the ore fluid during the mineralization. So, this is entrapment condition. So, what this diagram; how, we can use this diagram in retrieving the temperature.

So, considering the fact that this happens in a process of entrapment like the way we have depicted if we reverse the process for example, if we heat this particular inclusion while observing under the microscope by using our appropriate devices which I will not be discussing here for the sake of brevity.

And so, what exactly the expected here is that as we increase the temperature this is also going to follow the same path which it followed during the time of its entrapment and post entrapment phase change. So, the vapor bubble will gradually grow smaller and smaller and smaller and till the time the till it reaches the point here where the vapor bubble is going to disappear and it is supposed to follow the same further heating it is supposed to follow the same isochoric path.

So, the temperature at which the fluid becomes homogeneous from this condition to a point here where the vapor bubble will disappear we will call this temperature is the temperature of homogenization; that means, from a heterogeneous condition the inclusion attains a homogeneous condition and.

So, that we call it as a temperature of homogenization any further increase in temperature will make the inclusion follow this particular isochoric steep isochoric path and then when we further increase we do not have any constant to reach at P 1 T 1. So, there is the limitation.

So, the temperature corresponding to T 1, if we drop the perpendicular over here, this would be the temperature was temperature of trapping or the temperature of formation of the particular inclusion we say that it is the temperature of homogenization or the; and discarded is corresponding to the point at which the vapor bubble disappears.

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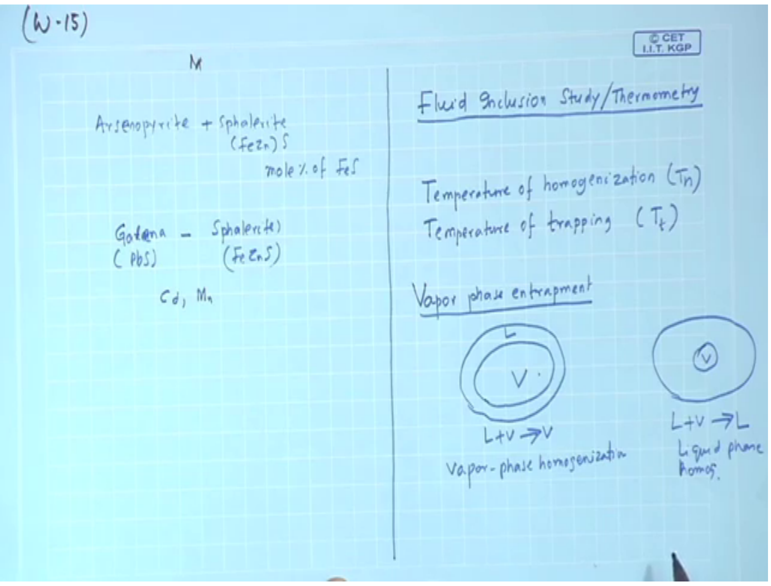

(W-15)

M

Arsenopyrite + Sphalerite
(FeZn)S
mole % of FeS

Galena - Sphalerite)
(PbS) (FeZnS)

Cd, Mn

Fluid Inclusion Study/Thermometry

Temperature of homogenization (T_h)
Temperature of trapping (T_t)

Vapor phase entrapment

And temperature of entrapment or temperature of trapping which we represent as dt and so, here and here actually what we are representing here that if we drop a perpendicular from here this will be the temperature of homogenization that is Th and if we drop a perpendicular from here it will intersect the abscissa on the point which will be Tt and there will be difference some difference of the temperature between the temperature of between the Th and Tt.

So, if we are relying on only this experiment then we will be missing the temperature of formation or the temperature of trapping by a few degrees and its all depends on the slope of this isochore will tell is to how much will by how much we will be missing the actual temperature of formation, here, if we if we have any independent consideration of temperature or pressure.

For example, if we are carrying out this fluid inclusion exercise on a particular mineral which itself can indicate pressure like sphalerite which whose composition is an is a is a function of pressure mole percent of sphalerite under a certain conditions is sensitive to pressure and the pressure could be determined and if we are doing this fluid inclusion exercise on the mineral like sphalerite or any other mineral for that matter which can indicate pressure.

Then we have a constant to to stop here or to get this particular point of a pressure trapping and from which we can draw a perpendicular on the excesses to get the temperature of trapping. So, this is the story of a single fluid inclusion and we actually measure a innumerable number of such inclusions in it in a in a in a roll body to get a a range of a temperature for the formation for the for a mineralization process and that that gives us a. So, first of all when we talk about the fluid source and we have we have we have characterized the different fluid sources like pituric magnetic metamorphic juveniles and so on.

We can get some fastened information as to what kind of a fluid we are essentially dealing with by the time we are finishing the micro thermometry exercise on a large number of inclusions on the minerals that we have taken from an ore body this is a very simple diagram, but the fluid crustal fluid this very complex mixture like if we see this table.

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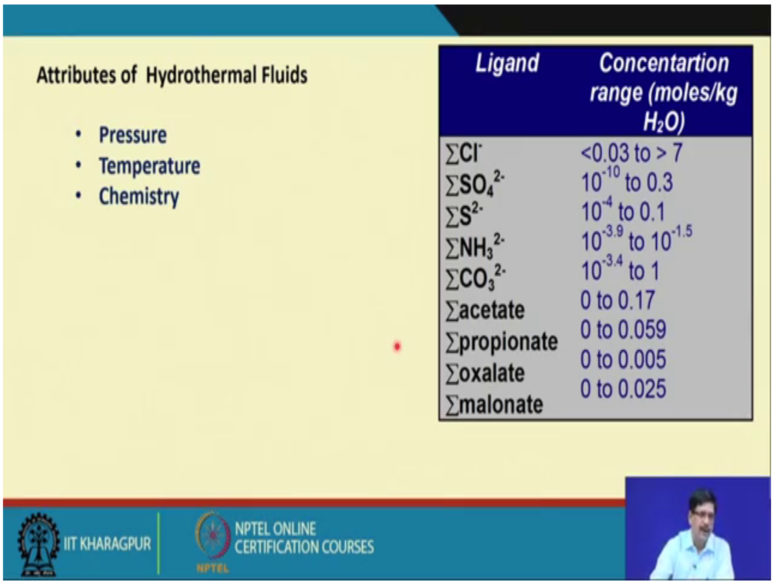

Attributes of Hydrothermal Fluids

- Pressure
- Temperature
- Chemistry

Ligand	Concentartion range (moles/kg H_2O)
$\sum Cl^-$	<0.03 to > 7
$\sum SO_4^{2-}$	10^{-10} to 0.3
$\sum S^{2-}$	10^{-4} to 0.1
$\sum NH_3^{2-}$	$10^{-3.9}$ to $10^{-1.5}$
$\sum CO_3^{2-}$	$10^{-3.4}$ to 1
$\sum$acetate	0 to 0.17
$\sum$propionate	0 to 0.059
$\sum$oxalate	0 to 0.005
$\sum$malonate	0 to 0.025

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This is a; this gives us some idea about the general chemical characteristics of hydrothermal fluid we see that it actually represents the whole spectrum. So, where the concentration of a chloride ion can go from point zero three to could greater than seven moles per kg sulfate ten to the power minus ten to point three sulfide NH3 carbonate acetate propionate oxalate malonate this is a giving a way, it is of course, not exhaustive list of the chemical species that there could be present in a hydrothermal fluid.

But it is a very complex mixture of many dissolved solids anions and cations and this gives us an idea and from that we can know that what kind of what considerations, we have to take when we actually are dealing with the actual a real hydrothermal fluid which is much complex the brain and a complex mixture of many different phases and we have to understand the phase relations in many such systems and from that we can interpret our data on the thermo thermometry.

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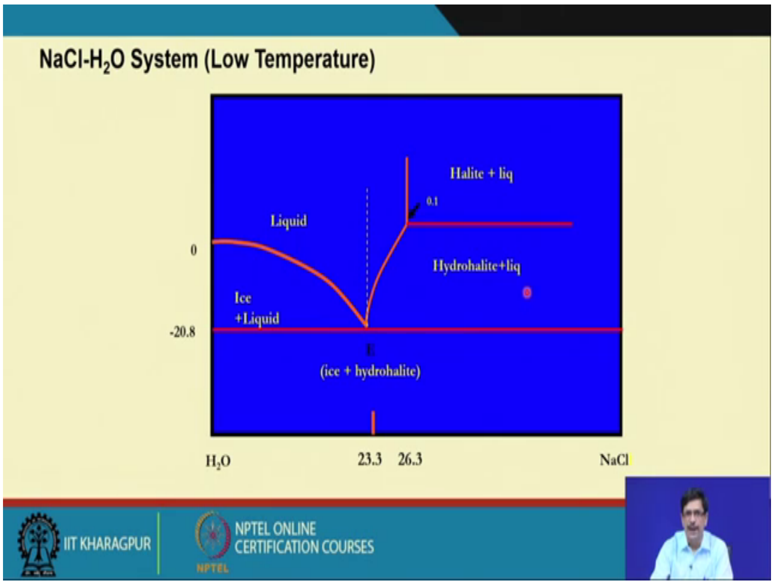

NaCl-H_2O System (Low Temperature)

The characteristics of the hydrothermal fluid in terms of the source we also characterized by the salinity and as we saw just on the table that a chloride constitutes the dominant anion in many in many of the hydrothermal fluids that we sample in different types of deposits these diagrams. This figure gives a very good idea as to how we can estimate the salinity in terms of the total dissolved solid of any hydrothermal fluid which is sample from the fluid inclusions in minerals.

Similarly, we can the way we contact the heating experiments we can also contact the quick freezing or the cooling experiments and use very simple principles of colligative property of depression and freezing point to constrain the salinity or in terms of which is expressed as the weight percent equivalent of a in a CL, here it is a part of a phase diagram of water and a cell binary where you where you can see the temperature at which pure water freezes at zero degree centigrade and this particular cotectic curve represents the depression in the freezing point of the of water with increasing content in sodium chloride.

And on a binary this temperature represents eutectic temperature corresponding to 223.3 weight percent of NaCl and minus 20.8 degree celsius and on the NaCl rich side, this cotectic represents the; so, the this cotectic essentially represents the ice plus liquid curve in which the with increasing with the decreasing in temperature the liquid becomes richer more concentrated with respect to sodium chloride and as and when the point eutectic e is reached the solid which is your sodium chlorite plus 2 H2O that is hydro halide will form along with ice.

And it is on the NaCl rich side its already forming ice hydro halide plus liquid and the liquid is becoming less and less concentrated with respect to NaCl and as it when it reaches the eutectic temperature both solid hydro halide and I specialize and if we consider the liquid which are essentially under saturated or not saturated with sodium chloride like the example which you took just before while discussing the heating experiment. So, we can do the experiment and freeze the inclusion and see at what exactly at what temperature the ice melts and we will be able to find out what percentage or what weight percent of sodium chloride equivalent amount of sodium chloride will cause that depression in the freezing point.

And we can determine the salinity of this fluid. So, likewise we determine the solidity of a huge large number of inclusions aqueous inclusions which are present in the host minerals the host minerals could be quartz or any other host mineral or even sometimes it is also possible with some specialized techniques to study the fluid inclusions in opaque minerals also and can retrieve such information on the salinity and temperature characteristics of the fluid as constraint from this fluid inclusion study.

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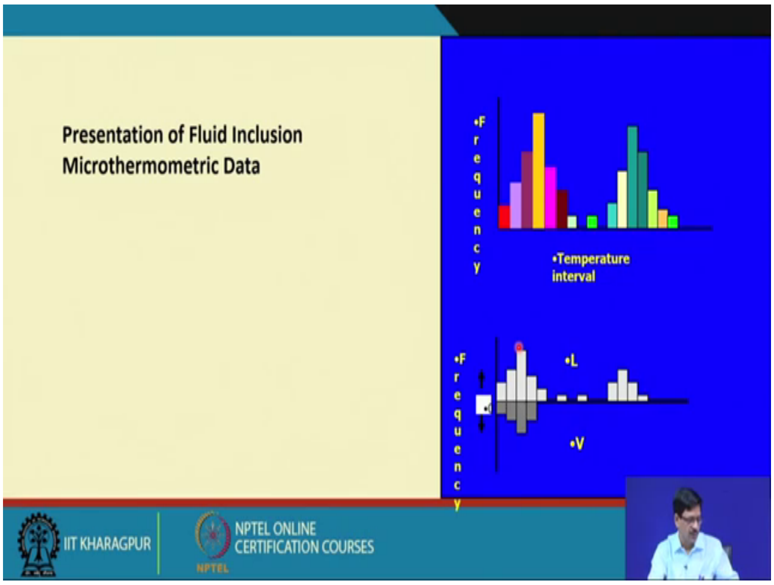

Presentation of Fluid Inclusion Microthermometric Data

We can represent the data because this is just for a for an example because we can; once we measure a huge population of such inclusions we get ranges of temperature and we would like to plot them or represent or present them on a statistical making a some statistical sense and we plot them a histograms and then find out that whether this fluid is essentially is coming from a one such population or coming from more than 1 population with modes or the temperature maximum more than 1.

So, this also gives us some preliminary idea about the process that is involved and if you remember we in one of our previous discussions, we saw that these hydrothermal mineralization process even though we identified many different fluid components, but the process sometimes involves involvement of a more than one fluid types and it happens because of fluid mixing process it will be discussing in a short while. So, this is the way we can represent the fluid inclusion micro thermometric data this is a diagram of which it is shown that the homogenization that we get could be of two different modes.

The homogenization could be of the liquid phase or could be to the vapor phase for example, if the if the inclusion initially or the fluid was initially in a vapor; vapor state, then any inclusion which is trapped over here will essentially be trapping a vapor and with decrease in temperature that vapor rich inclusion will give rise to liquid and only difference will be that if it is a vapor phase entrapment, then we will goal we will only be getting an inclusion where we will be getting a large vapor bubble as compared to in a liquid liquid phase entrapment when we get a small vapor bubble.

So, in such kind of a situation here, but the homogenization behavior in this case is l plus v to l in this case it becomes l plus v to v or we call as vapor phase homogenization here it is liquid phase homogenization. So, this essentially the figure here is which is not shown here, but could be if the entrapment of the inclusion was in the in this field then the homogenization also will be to the vapor and the isochors will be in the vapor region.

And here what exactly we mean that if we get some such situations of which will; which I will be discussing in a little while in the next class that there could be vapor phase homogenization and we would like to represent what is the proportion or what is the a statistical statistically how many inclusions were homogenize homogenized into liquid phase or how many to the vapor phase and what temperature range to decipher something very important in that respect.

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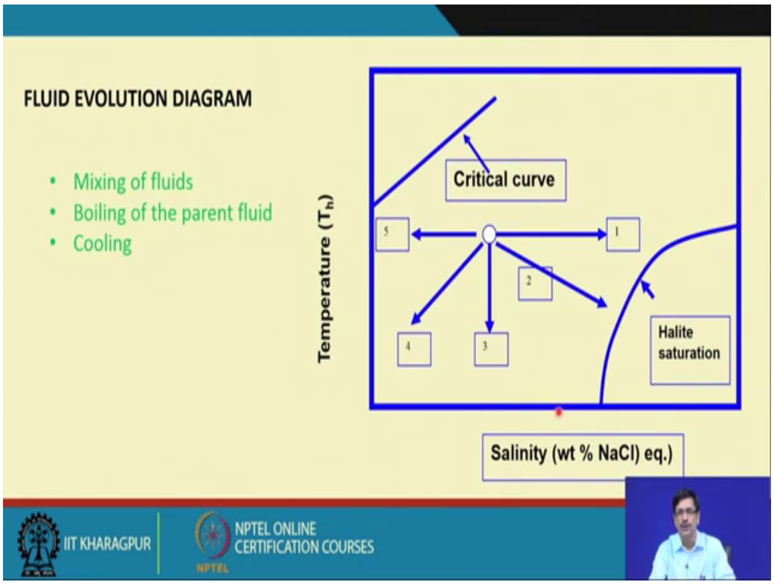

FLUID EVOLUTION DIAGRAM

- Mixing of fluids
- Boiling of the parent fluid
- Cooling

So, this in the context of the aqueous fluid this diagram which we which is constructed from a good number of for a substantial number or adequate number of fluid inclusions where the micro thermometric study has been conducted they are plotted on a temperature versus and the diagram which we essentially call as a fluid evolution diagram.

So, if we take a hypothetical fluid representing hypothetical fluid over here then we can have several possibilities when we plot the temperature versus salinity data; that means, the inclusions on which we have measured the temperature and also we have measured the salinity in terms of weight percent NaCl equivalent, we can plot them as scatter diagrams and depending on the nature of those scattered points we get certain well defined trends.

So, this trend is shown here on the horizontal arrows could be that they could be the mixing of different the mix of fluids of different salinity this particular trend would be for boiling this could be for cooling and this also could be for mixing. So, mixing of fluids boiling of the parent fluid and cooling or so, some such processes are very important from the mineralization process point of view and there its actually there in addition to the characteristics of the ore fluid it also is very important to know that how the fluid actually evolved because that actually caused the process of deposition of the minerals which will see them which we will continue discussing in the next class.

Thank you.