Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application
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Lecture – 17
Pure Carbonic Inclusion (Contd.)

Welcome to today's lecture, we will continue discussing on the carbonic fluid inclusions, and their use, and what the information that we retrieve from them.

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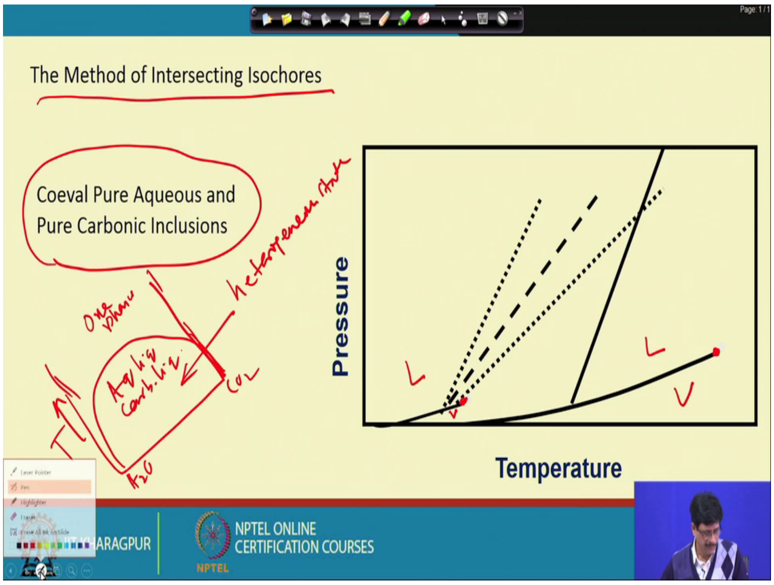

The Method of Intersecting Isochores

Coeval Pure Aqueous and Pure Carbonic Inclusions

We just discussed about the density, the carbonic inclusions their behavior to micro thermometric experiments, calculation of the volumetric properties density and their isochor.

Now let us see this consider the situation as to how we can use the data of these carbonic inclusions for thermo parametric? In fact, it becomes much easier or in this case we will consider the thermo parametric exercise; thermo parametry essential we mean that we should be in a position to and determine; deduce the temperature pressure condition of entrapment.

So, here this is a schematic diagram on which such kind of a thermo parametric exercise has been shown. And as is the heading here it is a method of intersecting isochores. Isochores again at the reiterate that they are the path of constant density constant composition and which the inclusion has retained its volume has remain there is a close system and evolved in p t space.

So, this diagram here is drawn with both carbon dioxide and the water unary system combined together. This the water where it is the liquid field of water and this is the vapor field of water and here it is also the liquid of carbon dioxide and this vapor and we know the super critical region. So, here what we see here that these are the isochores of course, it is only one drawn, but we can also have when you more of such isochores for this liquid inclusions also.

So, the condition is that we must have coeval pure aqueous and pure carbonic inclusions; if you remember then all the binary of H 2 O and CO 2; we know that the salvers is like this. And this is corresponds to any particular pressure and this is temperature and this is the mole fraction of carbon dioxide.

We know that this is the one phase one phase liquid and this is 2 phase that is the aqueous liquid that is a carbonic liquid or carbonic carbon dioxide could be in vapor depending on where which design we are in. So, in the situation corresponding to this 2 phase condition in which there will be an aqueous liquid and a carbonic liquid. That means, the fluid that we are considering is in heterogeneous state.

But as before as for our assumption the entrapment is homogeneous means the host mineral which is going in presence of the fluid will trap either the carbon liquid or the aqueous liquid not a mixture of both. So, under that circumstance what we will see what will see there that like as before.

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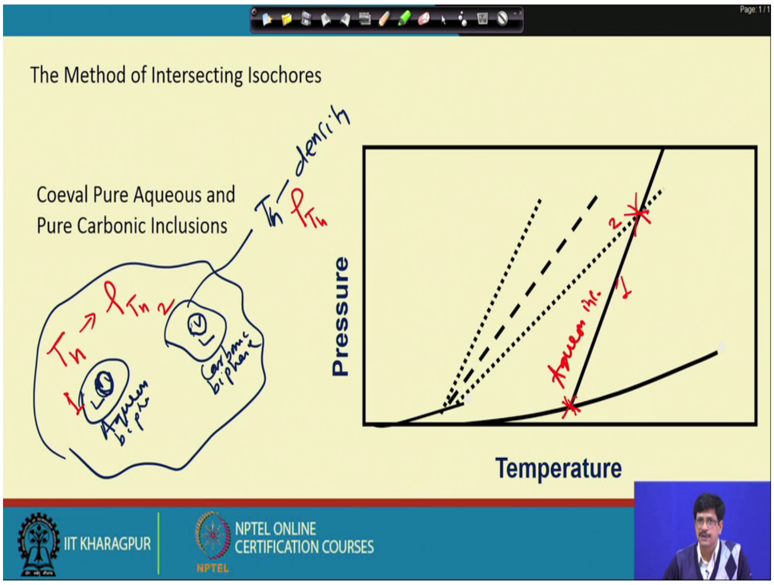

The Method of Intersecting Isochores

Coeval Pure Aqueous and Pure Carbonic Inclusions

If this is a host mineral let us say quartz. So, within that there is one inclusion this is a; let us say this is a aqueous by phase inclusion. And this is a carbonic by phase inclusion; this need not necessarily have to be by phase it could also be a mono phase, but it should at least give raise to a vapor on cooling few degree from the room temperature.

And we should be able to note down the T h liquid vapor for this particular inclusion and also calculate the density in term. Similarly we should also be; similarly this is the aqueous by phase and we also should have determine the T h liquid vapor homogenization. And also it is a salinity and then that would have made that would have allowed us to calculate the sum the density that is the rho at T h; similarly this also the density as rho at rho as T h.

So, these inclusions these 2 it is necessarily have to satisfy the condition of coevality; means they must have been trapped at the same time by the growing crystal as a part of the three demisional report or may be that if their or a particular hilk crack. It depending one particular generation of an inter pantavercy secondary fluid it also could be possible. But, the first case is more appropriate or is mostly considered, and then this case this both aqueous liquid this aqueous liquid by phase inclusion. And the carbonic by phase inclusion were trap at the same time to the coeval.

So, once I have the density for these 2 density inclusions known; I can plot the one can plot the isochore of the aqueous this is the isochore of the aqueous inclusion. And suppose this dot this line this particular line; this is line 1 and this is line 2 are corresponding to inclusion 1 and inclusion 2 here.

So, then so as expected since carbon dioxide will is a lower density fluid lower density liquid here compared to the aqueous liquid of a specified weight percentage this L. Then the aqueous liquid isochors is likely to have a steeper dp by dt slop compare to 1 which is for the carbonic liquid. So, they are definitely go in to inter sector in space; if we extend the isochors, because once we know this once a temperature homogenized. And this is for the liquid; aqueous liquid inclusion this for the carbon inclusion known and the isochors are constructed and the isochors are intersecting in this particular point.

So, the point at which the isochors are intersecting will uniquely define the pressure and temperature condition of formation of this particular mineral as well as the temperature and presser of the fluid. Now the situation is that in a particular grain there may be several such instances. Or in course of study of the samples taken from the entity that we are interested in the inclusion from aqueous from a mineralize gain and anything of our interest. Then we would done 6 such kind of and these inclusions which we classified than the beginning is getting arise according to do way these scheme we have followed.

Such way distance is noticed in many different instances that you can have; several such inter section points if we take all the inclusions aqueous in all such coeval pure of aqueous in carbonic inclusion. And then you can plots them in the pretty space and can get the complete spectrum of evolution of the fluid in terms of the pressure and temperature.

So, this is one of the practices which is commonly followed in fluid inclusion thermo barometry ok.

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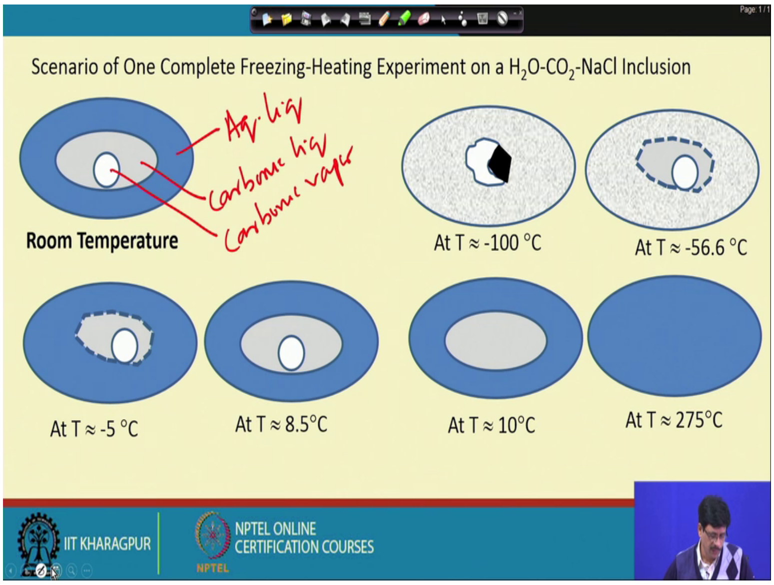

Scenario of One Complete Freezing-Heating Experiment on a H_2O-CO_2-NaCl Inclusion

Room Temperature

At T ≈ -100 °C

At T ≈ -56.6 °C

At T ≈ -5 °C

At T ≈ 8.5°C

At T ≈ 10°C

At T ≈ 275°C

So, from the pure carbonic inclusion we logically we should switch over to situation which are the mixed aqueous carbonic inclusion, where we remember it is basically is the aqueous liquid, this is the carbonic liquid and this is the carbonic vapor.

We have understood the interrupt and condition temperature and pressure condition in relation to phase diagram phase relations in water CO 2 system, where the water is not a pure water as we consider them as CO binaries a water of a fixed Anasil weight percent can be understood of the phase behavior of that particular water inclusion to carbon dioxide as to what is the mutual solubility or miscibility between them can be studies as CO binaries. And we know them that exactly from the civics of diagram we saw before. We know what are the miscible resign, and what are the immiscible resign and occurrence of such kind of aqueous carbonic inclusions commonly as it as a uncounted in many environments.

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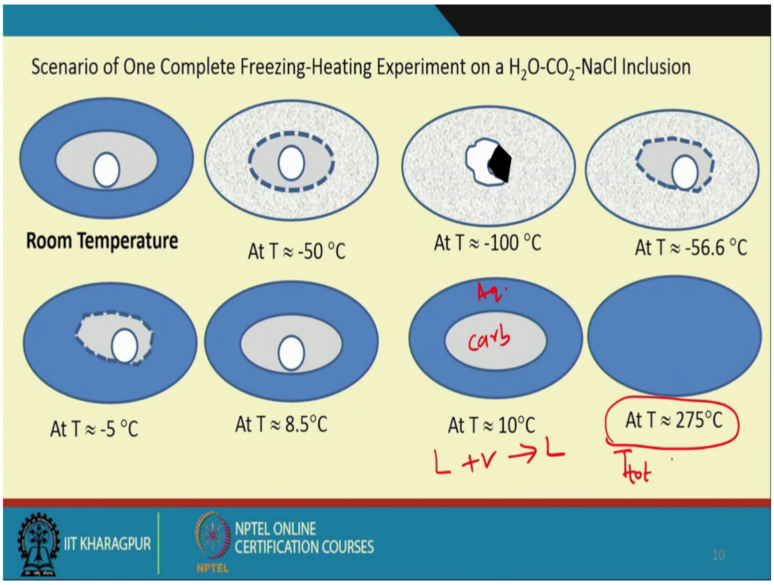

Scenario of One Complete Freezing-Heating Experiment on a H_2O-CO_2-NaCl Inclusion

So, now we will see the response of these inclusions to a freezing cycle; freezing warning cycle; this car this is the aqueous liquid and this aqueous liquid is likely to or a suppose to be responding the way which we have seen for aqueous by phase inclusions, pure aqueous by phase inclusions. Where, we know you can be explain on the basis of the binary and this super cooling and the things discuss before.

Now the difference is that this aqueous liquid has got a carbonic liquid and a carbonic vapor within that. And the pressure in temperature at which the inclusion is if the temperature of course, room temperature, and the pressure at which the inclusion is basically decided by the vapor pressure of carbon dioxide at that particular temperature because both liquid and vapor are there.

Now if you freeze this inclusion; what we should expect? We would expect that the aqueous part to freeze first. And as we know it will require super cooling and these aqueous part; suppose if I say that this is a 10 of 5 weight percent an NaCl equivalent, then this suppose to solidify at temperature anywhere between minus 20 to minus 2.5 or so.

But as we know it will not do so, it will require requires super cooling for that to become solidify. We know that this solidification temperature or the triple point of carbon dioxide is minus 56.6. Ideally also this liquid this carbon dioxide liquid plus vapor should solidify at that temperature, but that will also not happen, because of the super cooling that to be required. So, often we freeze this freeze this a inclusion let us say we see what happens at minus 50 degree Celsius.

Suppose this aqueous part which would have solidified corresponding to the eyes liquid quoted take at some point between minus 2.5 or so of the; you technique of the minus 20.2 will not do so and it will; it will solidify complete become frozen at over minus 50. So, that time because of the expansion of these solidification of this aqueous part these carbonic; the boundary between the car carbon dioxide liquid and the aqueous liquid will become defuse and but still we will be able to see the vapor within that.

These vapor of course, would not be executing much of a pseudo movement because the temperature has been much low and there is no much of terminal agitation for the vapor to move in side. Now this corresponds to a temperature which is about minus 100. Now what is happened in that these particular liquid carbon dioxide part has solidified and is become a solid like a half moon shaped solid ice which is distinctly white in color and this dark part is actually the vapor which is distorted in its shape, because of the solidification of this liquid carbon dioxide. But as not the volume has not decrease, but it would rather have slightly increase because of this is because of the positive dp by dt slop in case of carbon dioxide.

So, this is the state in which the inclusion is completely frozen. Now let us warm up warm the inclusion up at a control heating rate. And then as an when you are reproaching about minus 57 or so this solid carbon dioxide is will start melting. And if keep the minus 56 for the temperature fixed at about minus 56.6, we will see that this particular carbon dioxide is melted and is come back to the liquid plus vapor situation.

Now this is situation which; which is shown at minus 5. So, minus 5 is a situation where let us say depending on the weight percent (Refer Time: 14:59) equivalent of this, this has become this last ice in this particular liquid phase also melted. And it is kind of comeback to its original composition of the liquid composition that we started with. And then we are again increasing the temperature and see let us say there is a temperature would 8.5.

And this is the description is a absolutely a very schematic it is; it will usually whenever we do work on a car aqueous carbon inclusion, this behavior it is definitely expected keeping a side the possibility of the meta stability which can lead us to anything it. The meta stability could be such that is inclusion does not even response to even minus 196 degree Celsius, and those are those are exceptional cases. But I am this description is absolutely ideal as you would be expected in a heating freezing cycle; freezing heating cycle for a carbonic aqueous carbonic inclusion.

So, why I am showing it by a 8.5; so when the temperature is about 8.5 degree Celsius; I could see that this inclusion is now coming back to with exactly the shape or the kind of phase combination these from where we started. The situation is as compared to the situation at minus 5 where the meniscus of the liquid water and the liquid carbon dioxide is still very diffused and started or in a deformed state. Suddenly I find this particular meniscus is become very clear and the bubble with the carbon dioxide vapor bubble will also started to execute this suede gram movement.

So, this temperature is something which is very significant. Now at 10 degrees this is about 10 degree Celsius. Now where this 10 degree Celsius corresponds to a temperature of liquid vapor homogenization of this; that is what the partial homogenization of the carbonic part; here I see that the carbonic liquid and the vapor homogenized in to single phase. So, L plus V to L this is happened at 10 degree Celsius and now this inclusion is heated to higher temperature and that is say it around 275 degree Celsius; I see that this is become a single phase carbonic single phase inclusion.

Now, what is happened here? If we remember the situation what we which illustrated that this particular in case of a liquid plus vapor by phase situation; in this situation also this is the carbonic part, this is the carbonic part and this is aqueous part. And the homogenization the way it is happening actually. The carbonic part will gradually becomes smaller and smaller in its size and disappear, this is exactly as it happens in a liquid plus vapor to liquid homogenization in a by phase inclusion.

So, this carbonic phase will shrink or will decrease in its size; this will happen because of the increase mutual solubility of carbon dioxide net and water among themselves. So, exactly the same thing will happened it disk to a just around the time of the liquid the carbon dioxide liquid which it is substantially decrease in its size; it will also execute bigger as pseudo movement and will disappear at the point at a temperature.

This temperature at which it is it disappears at 275 degree Celsius will say that this is under gram a total homogenization or T total; T total. So, we can say that this is; so now situation is that in all the cases it may not be that it is homogenization to T total to liquid perceive is say that is here this homogenization is. So, the homogenization is L aqueous plus L carbonic to L aqueous means it is homogenized to an aqueous face.

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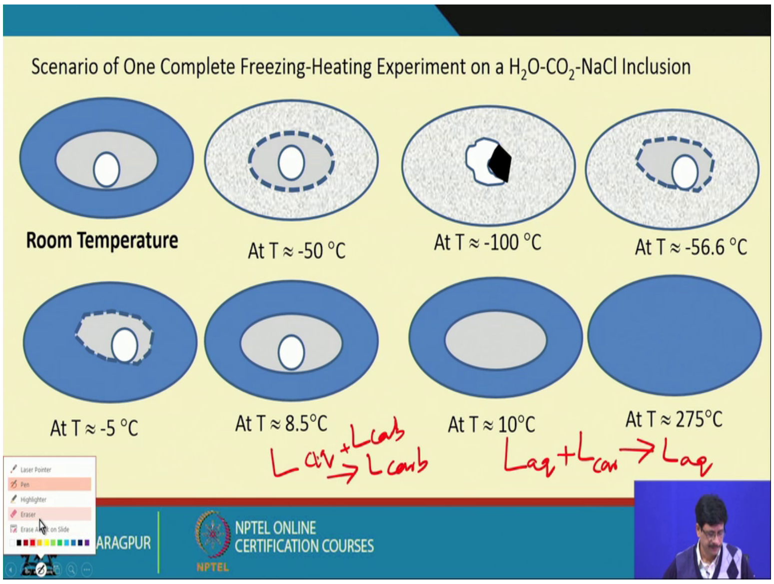
Scenario of One Complete Freezing-Heating Experiment on a H_2O-CO_2-NaCl Inclusion

$L_{aq} + L_{carb} \rightarrow L_{carb}$

$L_{aq} + L_{car} \rightarrow L_{aq}$

The other situation is also possible means this carbonic part which is shown here; may also expand in its volume and fill up the cavity fully and that could have been a situation where L aqueous plus L carbonic to L carbonic; we will discuss the situation little later.

Now, so here what actually I have missed in the discussion I will now try to fill that up. As we know this carbon dioxide is a very unique carbon dioxide net water or it is gasses like carbon dioxide and methane. They do have unique property of absorbing a water molecules and forming something which is called as the hydrates gas hydrates or.

So, in case of carbon dioxide there call the clathrate and this is a carbon dioxide clathrate.

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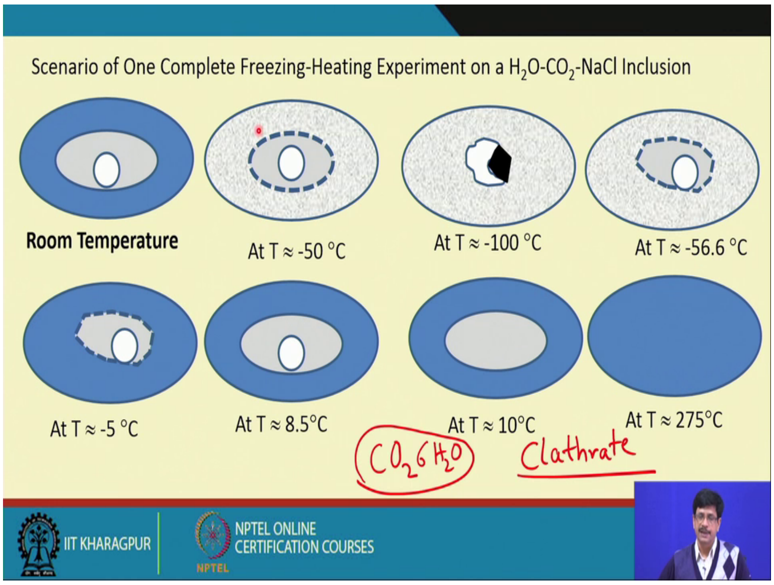

Scenario of One Complete Freezing-Heating Experiment on a H_2O-CO_2-NaCl Inclusion

So, the composition could we something where you roughly CO 2 6 H 2 O; sometime we can see if 5.7 H 2 O 6 H 2 O; sometimes there are the socio matrix is also differently put in sometimes we will could be 8 H 2 O.

So, the fact is that the carbon dioxide component here can absorb can unique and combine with water molecule in a ratio of 1 is to 6 nearly, and can form these solid which is the hydrate the clathrate; so, is known as the clathrate. So what is expected here? That these clathrate when the temperature is being decrease from room temperature to any lower temperature, so this carbon dioxide in combination with this water is supposed to form the clathrate from temperature which is in the positive range of 10 degrees or even lower.

So, it is not exactly very easy to pin point all the time when exactly the clathrate is forming because the clathrate is a colorless white solid. And it will always get mast with the frozen characteristic of the liquid or the freezing of this liquid part. But it is most likely even also the kind of laboratory experiments which we are doing; where we are cooling at a much higher rate and in the in the heating freezing apparatus.

It might be that it would also be a kinetic factor in which the hydrate may be just farming, on the contact of the on the meniscus, on the liquid and carbon in 2 liquids. Or would have also if these particular when we are seeing the there is already carbon dioxide and water and we know the room temperature solidity of carbon dioxide and water is a 2.3 mol percent to; some deserve carbon dioxide is also there.

So, whether they also do form the hydrate or not it is not very well known and it is also very difficult to know in normal by bio thermometric experiments. So now, what we could basically can have is that at around the situation that talking about; when the situation is such that the last ice has melted in the aqueous part. So, the last ice in the; so one of the important implication here is that if the carbon dioxide has taken up water in the proportional 1 is to 6.

So, this particular aqueous liquid will be depleted with respect to water or in other words the sold concentration will be apparently more in this liquid when some water molecular has been. So, depending on what how broad or how thick of groom of clathrate is forming here; whether this entire liquid is forming a clathrate it is not known. Because if the entire liquid has formed a cloth rate and at temperature corresponding tools set down minus 100 when this carbon dioxide is solidifying; it must be the release in the water because its solid carbon dioxide without any water in it.

So, to the best of the best expected this movement could be that may be that the clathrate forms at some kind of an inter face boundary to a forming a layer. And the rest in the amount any amount of water to come through that barrier also be difficult only when if it is kept at a much lower temperature for a very long time may be the entire material might become clathrate. But in a macro thermometric explained what would we expected is at even if the clathrate is formed. This part of the carbon dioxide has solidify and this phase change is so significant and so conspectus at it will not we missed by anybody when the carbon dioxide solid forms.

So, it forms with a very significant and also the carbon dioxide solid distinctly white solid. So now, when at this point of minus 5; this part the aqueous part has undergone the last ice melting. So, what remains here is a combination of vapor carbon dioxide, liquid carbon dioxide, clathrate and the aqueous liquid; so it is a kind of a 4 face assemblies we can tell.

So, now what happens the clathrate is melts. Let us say the clathrate is will see now at this clathrate carbon dioxide clathrate for a pure. Now if this particular water is pure water then this clathrate would melt the 10 degree Celsius; if the water contents electrolyte like solidum chloride to variable percentage then the clathrate melt melting is depressed; which will just see in the next diagram.

So, what will happen here is that at 8.5 degree Celsius, this defuse boundary will become very confucusly a very clear boundary with; now because of the depending on the size of the vapor and the liquid in the carbon dioxide part. We see that at least this particular liquid meniscus will get back to its original sharp nature compared to kind of a defused at distorted meniscus boundary when cloth rate was there. And, then rest of the thing which we have already discussed ok.

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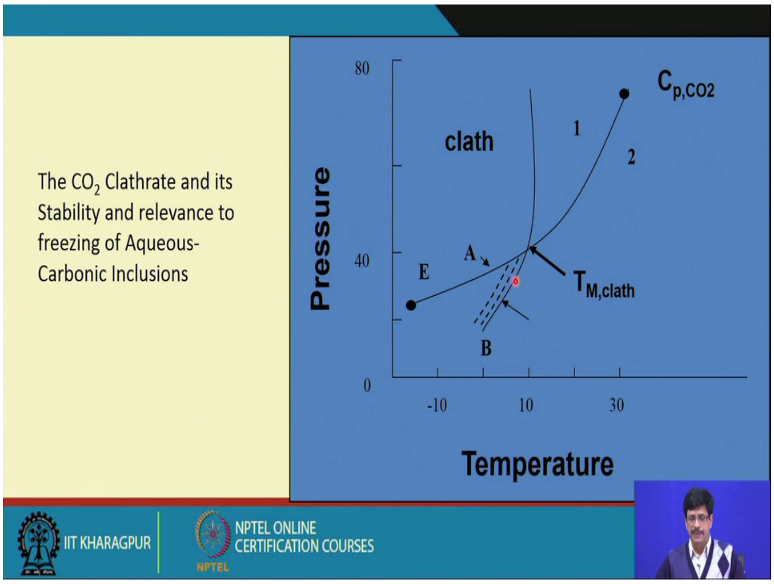

The CO_2 Clathrate and its Stability and relevance to freezing of Aqueous-Carbonic Inclusions

So, this phase diagram is when the easy one to actually understand we can there are many more such later talk which people can refer. But to begin with this is very if the diagram which can be easily understood. This particular regain here is the clathrate stability, this is the carbon dioxide liquid vapor curve c critical part of carbon dioxide; 1 is for liquid and 2 is for vapor. Now this is the clathrate stability and we see the temperature corresponding to temperature which is shown here there is 10 degree Celsius over here.

So, we see that if its carbon dioxide if the water is pure; so, here this corresponds to that particular 4 phase assembly freezing which we have been aqueous liquid, carbonic liquid, cloth rate and aqueous a carbonic liquid carbonic vapor then aqueous liquid and cloth rates here it will melt. So, that this curve which goes from here to here goes up to the ternary eutectic which is almost would minus 20 or so.

Then the carbon dioxide water and and NaCl. Now if it contents this line this curve is essentially is the depression of clathrate disillusion or clathrate melting depression in clathrate melting with increasing concentration of sodium chloride. This 2 doted curves represents the suppose this point is exactly at these point the clathrate would melt at something less than 10, less than till with increase the concentration of sodium chloride you can go to the value of almost minus 20.

So, theoretically the clathrate can melt at pure aqueous liquid pure aqueous carbonic situation, where the clathrate could melt at 10 degree Celsius. Depending on the weight percent NaCl in the aqueous part the clathrate melting can get depressed can go up to a maximum minimum of minus 20; corresponding the term dejected to almost about 19 20 percent NaCl.

So, now we can realize that it will not advisable to calculate the salinity of the aqueous phase form the last ice melting in the aqueous phase. Because that is go to give us the erroneous value for this salinity of the aqueous face. And since there is a well defined if you could see it from a here.

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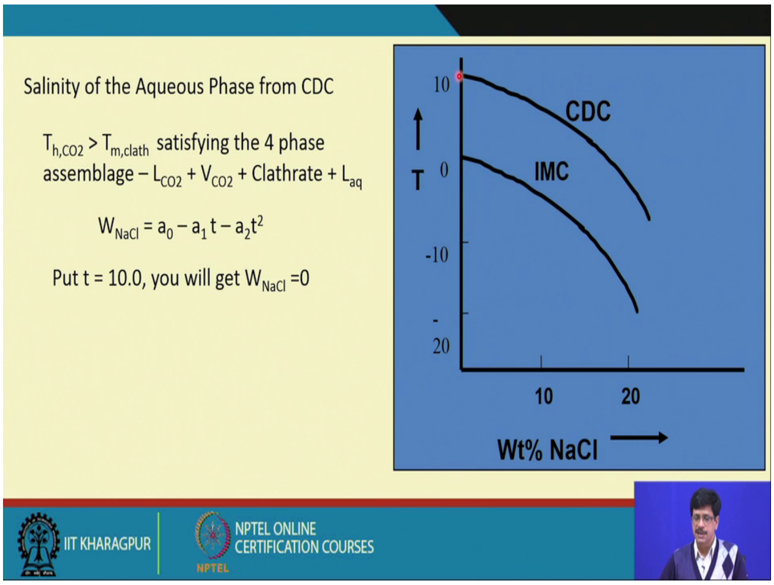

Salinity of the Aqueous Phase from CDC

$T_{h,CO2} > T_{m,clath}$ satisfying the 4 phase assemblage – $L_{CO2} + V_{CO2}$ + Clathrate + L_{aq}

$W_{NaCl} = a_0 - a_1 t - a_2 t^2$

Put t = 10.0, you will get W_{NaCl} =0

And this is the top curve is the clathrate dissolution curve this CDC and this the ice melting curve. As you could see the ice melting curve goes to about 23 or so you eutectic temperature of minus 20-21.2 and here the clathrate dissolution starts from 10 and goes an gets depressed and goes to can go to minus 20 degree Celsius.

So, then what one needs if you are to calculate the density, if the volumetric properties of this mixed aqueous carbonic fluid; then we need to determine the salinity of the aqueous phase. So, the salinity of the aqueous phase from the clathrate dissolution temperature is also fitted with the empherical equation with this a 0, a 1 and a 2 term being worked out; so W NaCl, this t is the temperature of melting of clathrate.

So, then here the situation is that we must have this particular point also gives a condition that these clathrate melting that that; the disillusion and cloth rate melting of the depression in cloth rate melting in only be used if it is a 4 phase assemblies. That is vapor carbonic; vapor carbon dioxide, liquid carbon dioxide, clathrate and aqueous liquid.

Now the situation if you if you are in the vapor stability field in this region 2; there we will miss the aqueous the carbon liquid part. So; that means, if the temperature of partial; partial homogenization temperature of that. This equation calculating the clathrate the weight percent NaCl of the aqueous part form clathrate dissolution temperature is applicable if T h CO 2 is greater than the T m clathrate. Means the situation which we described here that the clathrate is melted here by the vapor is present.

So, this is the condition n which it satisfied and we can calculate this salinity of the aqueous component form the temperature of dissolution of the clathrate; but, if the temperature of homogenization of carbon dioxide the parcel homogenization is less than that of the temperature of dissolution of clathrate. Now we have to look for different formulations. Like in this particular one if you put t is equal to 10, you will defiantly get W; NaCl is equal to 0.

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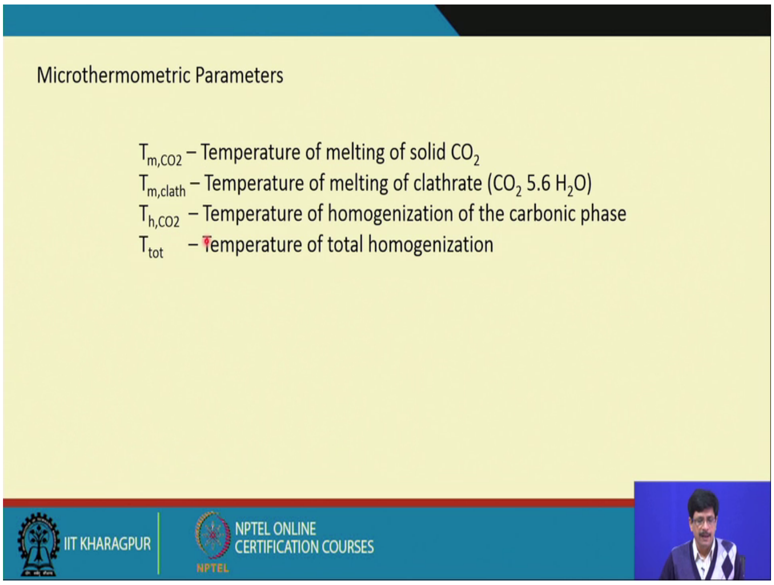

Microthermometric Parameters

$T_{m,CO2}$ – Temperature of melting of solid CO_2
$T_{m,clath}$ – Temperature of melting of clathrate (CO_2 5.6 H_2O)
$T_{h,CO2}$ – Temperature of homogenization of the carbonic phase
T_{tot} – Temperature of total homogenization

So, now see that the micro thermometric parameters that that are treated from the micro thermometric experiments on aqueous carbon inclusion that will to; we get T m CO 2, temperature of melting of solid ice we designate as T m CO 2.

And the temperature of melting of clathrate is T m clath, the T h CO 2 is the partial homogenization of the carbonic phase; either to liquid or to vapor. And depending on whether the homogenization is to the liquid phase; we can calculate density or using the formulation that we saw before, applicable for the liquid phase homogenization and also for vapor phase homogenization.

And this T total is the temperature of total homogenization; now the one of the thing to remember here is that these mixed aqueous carbonic inclusions are a bit difficult type of inclusion. Because in most of the cases we generally fail to get the total homogenization temperature; what we have depicted here the total homogenization temperature either to a L aqueous L carbonic to L aqueous because the mutual solubility of carbon dioxide and water is very much press dependent.

So, it would require higher and higher pressure for the dissolution this carbonic phase and aqueous phase of homogenization to give one liquid. And since, it all depends again on the power to for the host mineral to with stand the pressure is in case of a quartz it can we maximum with stand a pressure of 2 kilo bar. And so, what happens is that in most of the cases in case of larger inclusions; these inclusions; they generally leek, they generally the keep it at burst partially leak before the total homogenization is obtained.

In most of the cases actually get completely leaked and they do not come back their original position at all. So, these are the things that to begin with these are the important aspects of this aqueous even. So, even though there they are the most studied one and in terms of the system. These aqueous carbon these water carbon dioxide mineral cell system is been extensively studied in the steal been studied to understand the miscibility resign and to refine the formulations for utilization of the macro thermometric parameter in terms of thermo parameter which we will have a look in the subsequent class; in the next class.

Thank you very much.