Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application
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Lecture – 20
Microthermometry of Aqueous-Carbonic Fluid Inclusion

Welcome, to this lecture. We will continue our discussion on the Aqueous-Carbonic Inclusions and their implications to thermo barometry. We have discussed to some degree of details the procedure one of the procedures which you could adopt for calculation of minimum pressure of entrapment from the total the temperature of total homogenization with the compositional parameter of the aqueous component and the density of the carbonic liquid known and by and we as we say saw that this we calculation procedure is pretty elaborate. And, that has been many improvement many attempts to improve such formulations to get the accurate value of density and the dp by dt slope which actually is very important in understanding processes in which such kind of aqueous carbonic fluid.

And, we see the such kind of mixed aqueous-carbonic fluid is actually more dominant and deeper earth processes, whether it is metamorphism or mineralization and the interesting thing about this particular system and why is it very important is that there is a bit of a difference the fluid undergoes a drastic difference in it is chemistry when it splits from a homogeneous one phase condition to a heterogeneous to liquid condition and many processes like important because it also controls the solubility of many of the metals in such kind of mixed fluid.

So, it has got tremendous implications to understanding ore forming processes, where they the processes take place at temperature pressure conditions which are within these ranges that we are considering.

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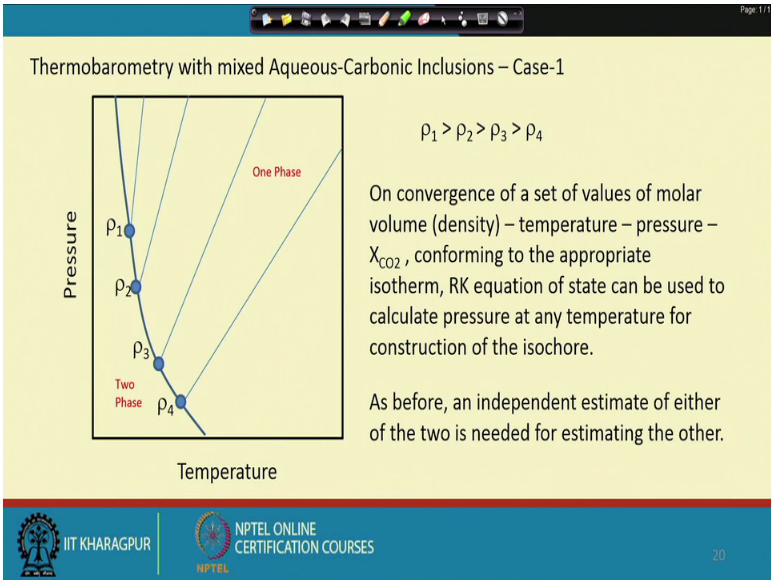

Thermobarometry with mixed Aqueous-Carbonic Inclusions – Case-1

$\rho_1 > \rho_2 > \rho_3 > \rho_4$

On convergence of a set of values of molar volume (density) – temperature – pressure – X_{CO2}, conforming to the appropriate isotherm, RK equation of state can be used to calculate pressure at any temperature for construction of the isochore.

As before, an independent estimate of either of the two is needed for estimating the other.

So, continuing our exercise on thermobarometry exercise on or thermo thermobarometric implications for mixed aqueous-carbonic inclusions. So, we just to recapitulate we can use the same logic that we have used for pure aqueous biphase inclusions or if any other inclusion, where the entrapment is homogenous and the heterogeneity the develops inside the inclusion cavity is a result of post entrapment phase change and we can determine the temperature pressure conditions as we did for a aqueous biphase inclusion by knowing the vapor pressure. In this case we are also able to calculate the pressure and the density of that inclusion by an elaborate method which we discuss before.

And, then as it happens suppose, the fluid is anywhere between anything to consider the row 1, row 2 or row 3 or row 4 where these are the row T as the total row total you can say that density total homogenization. So, they could have followed any of these isochore the way it is shown and the temperature pressure condition of entrapment could be anywhere on the isochore. And then it is that if we have any independent constitutional either temperature or pressure; that means, if you are working on an assemblies which is a good thermometer then both temperature and pressure could be could be found out from the once we know the isochore.

So, constructing the isochore, the accurate isochore in this H 2 CO 2 NaCl system is very crucial and we know that even though we are plotting you are drawing them as roughly as straight lines, but from the if we construct them the isochore from the modified release from the equation and there is a little bit of a non-linearity that will be there and they are rather would be more frontally curves rather than just straight lines in this mixed H 2 CO 2 system and so, this is one of the ways that temperature pressure could be obtained and any independent estimate of temperature or pressure.

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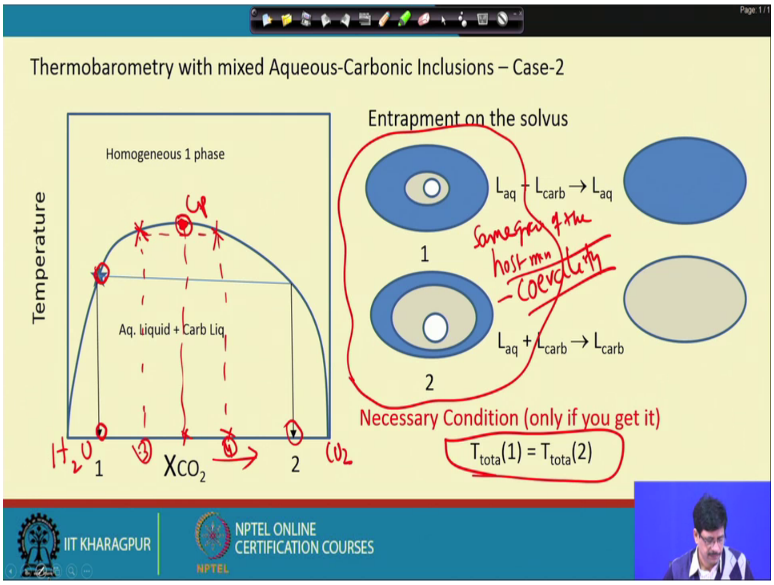

Thermobarometry with mixed Aqueous-Carbonic Inclusions – Case-2

Entrapment on the solvus

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

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

Necessary Condition (only if you get it)

$T_{tota}(1) = T_{tota}(2)$

Now, let us consider the another the situation in which we may not need any pressure correction or we the pressure temperature values need not have to come from any independent or we do not have to look for any other independent source of temperature or pressure. This situation is somewhat analogous to the situation which we discussed for boiling conditions in a aqueous fluid. So, what is boiling in an aqueous fluid the separation of a vapor phase can be thought of is it analogous situation here is that un mixing of a homogeneous aqueous-carbonic fluid to a heterogeneous combination of the two liquid or one of them carbon dioxide could be vapor depending on the pressure temperature condition that where we are.

These are essentially T - XCO 2 diagram. So, here we will consider a situation where the thermobarametry or the total homogenization temperature and the pressure calculated from that we will actually be the two temperature of two temperature or pressure of trapping. If we consider that the entrapment was actually taking place on the solvus say for example, here then this star represents the point on the solvus where the entrapment is taking place.

So, if the entrapment is taking place here the fluid is actually a heterogeneous to liquid fluid one like here it is a if we are doing it from an H 2O CO 2 and XCO 2 is increasing then we get one, you can calculate from the liver rule here that on this particular. So, this the fluid which is existing here actually is a mixture of two liquid, one liquid is mostly the H 2 O rich liquid with less of carbon dioxide and one here which is a carbon dioxide rich liquid with low with less of water which can be very well calculated by using the liver rule on this kind of a phase diagram.

So, corresponding if this is one then this corresponds to the inclusion which is shown here. A aqueous component which is more in it is volume and a carbonic liquid which is subordinate and it is also present is. Now, this particularly inclusion it homogeneous into in a aqueous mode, this L aqueous L carbonic becoming L aqueous means here after the parcel homogenization of this carbonic phase this with further heating the carbonic phase shrinks in its size becomes smaller and smaller and smaller. With, as we discussed the carbonic component would be executing pseudo brahmier movement very fast and it will homogenize and the clarity of the inclusion also allows us for a reproducible recording of the T total here it is homogenizing into liquid phase.

Inclusion corresponding to 2 is here we have to see an aqueous liquid which is much lower in its proportion volume, this is the carbonic liquid which is more in proportion and here when we do the micro thermobarometry we find that the aqueous liquid carbonic liquid is homogenizing into L carbonic. Means exactly if we remember what happens in a vapor rich aqueous inclusion by the homogenization takes place by expansion of the vapor and filling up of the whole cavity. Exactly the same manner this carbonic component will expand and will fill up the whole cavity that will be recorded is the temperature of total homogenization to the carbonic phase.

Now, here the necessary condition the that we apply here is that this two temperature the total homogenization situations as we described here has to be temperature which should be exactly same ideally or at least with a beta phase depending on the clarity of the inclusion or it is a essentially practical aspect that the determination of the homogenization into carbonic phase may not be that very distinct of that very well recordable reproducible in many of the situations. As you have said that data which are which will have to be some acceptable range of reproducibility can only be taken taking the ideal situation that here the temperature is also very well reproducible and the temperature of total temperature of total homogenization the T total in case of 1 is equal to the T total case of 2.

So, that gives us a very clear cut or a very definitive idea that the entrapment was hetro was from a heterogeneous mixture of the fluids, but entrapment was essentially homogeneous means the crystal when it is growing at one because it also has to abide by the same conditions that we put for the aqueous biphase. Inclusions means it has to be within the same these two inclusions, these two inclusions have to be within the same grain of the host mineral of the host mineral.

And, they also have to be a part of the random 3-dimensional network they are non trail bound and generally we say that I that there could be primary or their primary inclusions or let us say that they are this should be coeval at least they must satisfy the condition of coevality that they must have been trapped at the same point of time same conditions or president temperatures same point of time. So, that is how when they observable in a same single grain of the host mineral they will be part same as part of the 3-dimensional network in the solid lattice of the host mineral and then only we will in we infer that the entrapment condition was what we are visualizing here.

And, the pressure value that we determine here pressure and XCO 2 because XCO 2 is as visibly we know that they are going to be much different from each other in this case it much higher XCO 2 will be higher here it is lower and then the pressure and XCO 2 value corresponding to the temperature at which the homogenization took place can be taken as the pressure of trapping pressure and temperature of trapping. In this case we do not need any further correction to either of these two cases.

The as is clear from this particular diagram the entrapment could be anywhere on the solvus and even one can I mean it is theoretically possible that if it is if this happens to be the critical point. So, as I have said that entrapment or this situation could be anywhere on this solvus, even could be also a on the critical point.

Now, if we say that the entrapment was somewhere here, then the inclusions which are going to results. So, for example, this is inclusion number 3 and this is inclusion number 4. So, in that case inclusion 3 and inclusion 4 may not have very visibly different of very visibly distinctly different in the proportion of the carbonic to liquid carbonic liquids component. There may be very close by very at very similar, but then we find that in one case it is if they happen to be on the either sided because of course, they have to be have they have to be on the either side of the critical point.

So, in this; this is the aqueous rich part and this is the carbonic rich part. So, here the inclusion 3 and inclusion 4 may not have drastically different proportion of the two the aqueous and the carbonic component, still we can have the total temperature of total homogenization two different modes like the like once one here both to one to aqueous mode than on another the other to the carbonic mode we still the temperature of homogenization of this two being same.

Also, the situation is that you one can also have a condition pertaining to the critical point. So, it happens so, the critical point then we can have. So, here it is not possible to have these because it will be the if the entrapment on the critical point then we will have every fixed proportionally carbon dioxide to a aqueous component and the homogenization will be critical homogenization is both. In any or in a situation where we get many such aqueous-carbonic inclusion with comparable proportion of the aqueous to the liquid because it is a essentially the asymmetric solvus. So, we get the proportion of the aqueous to the carbonic component, they may differ and the homogenization is going to be on a critical mode.

So, critical homogenization mode as we know that in the critical homogenization the ripple bubble does not shrink to the minimum of the bubble size of a just a black dot and then disappearing rather the vapor bubbles shrinks or the decreases in it is size to a certain extent and after that the homogenization takes place by fading of the may discuss.

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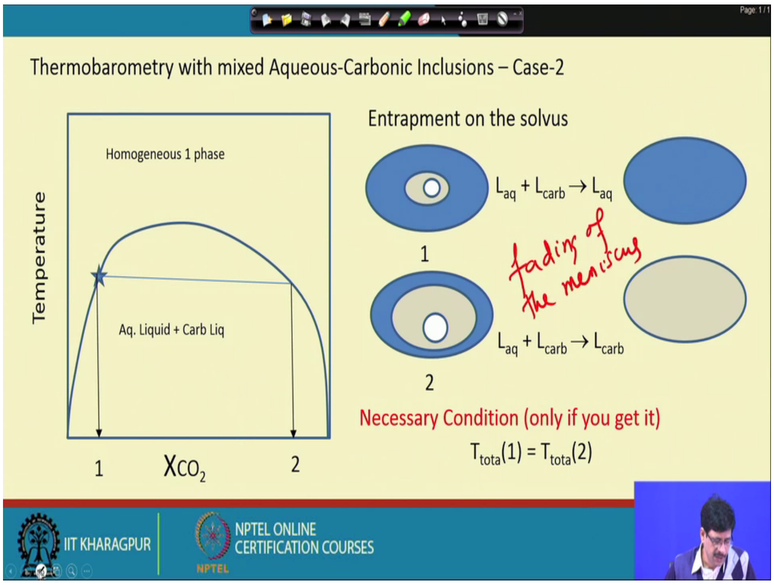

Thermobarometry with mixed Aqueous-Carbonic Inclusions – Case-2

Entrapment on the solvus

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

fading of the meniscus

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

Necessary Condition (only if you get it)

$T_{tota}(1) = T_{tota}(2)$

The just the boundary just become becomes in indistinct and they become homogeneous, such kind of a critical homogeneous in a very well observed in the aqueous phase inclusions. But, and ideally they also can be expected in such kind of mixed aqueous-carbonic fluid. So, that kind of brings us within the limitation of this particular lecture series the discussion on the mixed aqueous-carbonic inclusions and, their application.

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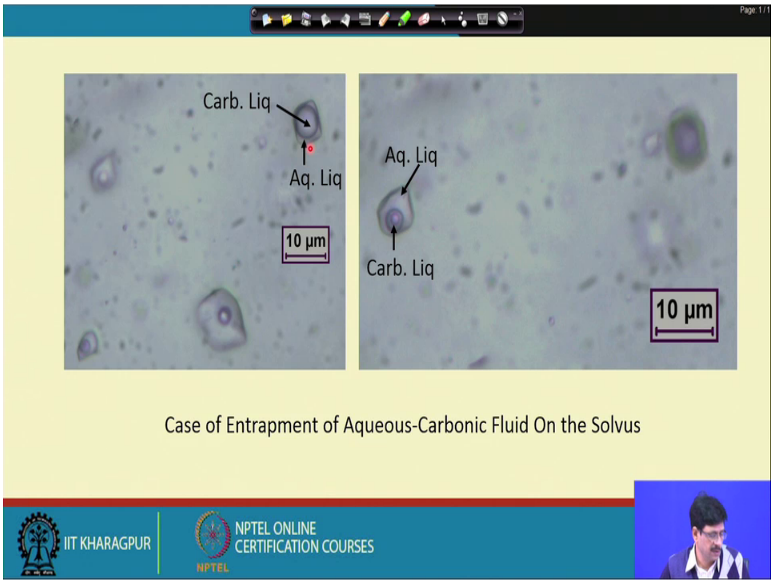

Case of Entrapment of Aqueous-Carbonic Fluid On the Solvus

So, what we can know about the fluid characteristics, this is again this diagram which I also showed before and you could see that in this case this particular inclusion which has the lower proportion of carbon dioxide is out of focus and so, that is why these two photographs which are from the same quartz, but taken at different focus presented here.

And, here you could see that the aqueous liquid is just a small part in the surrounding the carbonic liquid, it is a pretty regular shape inclusion where we can always take it to be workable regular inclusion regular shaped inclusion in which the data could be very well reproducible. And just within a with close special distance of it, but actually abiding by the rule that we apply that we can take for at least more than 5 times the diameter of an inclusion that we are seeing so, for the primary criteria. So, they do satisfy and here you could see the difference. So, in this case here the XCO 2 is low in this case is XCO 2 is high.

So, they do and then when we homogenize to be find that this homogenization is to the carbonic phase and this homogenization to the aqueous phase. In most of the cases even say we are talking about a situation like here where the liquid component is still lower we can also have that. This out of focus inclusion also has a still low value of carbon dioxide, but such inclusions are much more prone to decrepitation or leakage in the temperature is high this kind of inclusion which are just about 7–8 microns in it is maximum dimension these are the inclusions which are rather easier to work on and the obtained we can obtain the temperature of total homogenization and this kind of small sized inclusions and also we can get back to their original configuration.

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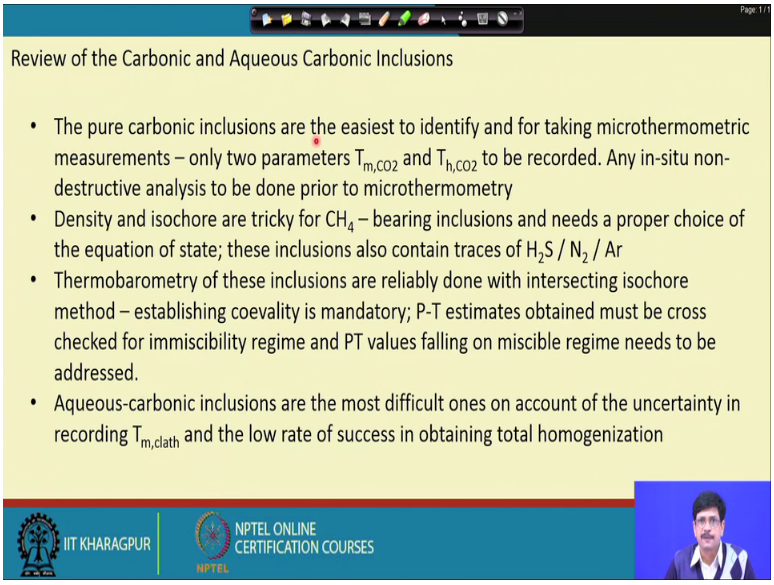

Review of the Carbonic and Aqueous Carbonic Inclusions

- The pure carbonic inclusions are the easiest to identify and for taking microthermometric measurements – only two parameters $T_{m,CO2}$ and $T_{h,CO2}$ to be recorded. Any in-situ non-destructive analysis to be done prior to microthermometry
- Density and isochore are tricky for CH_4 – bearing inclusions and needs a proper choice of the equation of state; these inclusions also contain traces of H_2S / N_2 / Ar
- Thermobarometry of these inclusions are reliably done with intersecting isochore method – establishing coevality is mandatory; P-T estimates obtained must be cross checked for immiscibility regime and PT values falling on miscible regime needs to be addressed.
- Aqueous-carbonic inclusions are the most difficult ones on account of the uncertainty in recording $T_{m,clath}$ and the low rate of success in obtaining total homogenization

So, a short review of what we can what we discussed about the mixed aqueous-carbonic inclusions. So, the pure carbonic inclusions are actually the easiest to identify, because as I said that since they would be very much close to their homogenization temper if we have seen them in room temperature in y phase mode; means there they will be homogenizing within that temperature of suppose we are maintaining room temperature of 25 degree Celsius. And the critical homogenization is 31 so, when we were seeing a y phase condition of a pure carbonic inclusion at 25 degree centigrade means it is quite close to it is homogenization temperature there so, the pseudo Brownian movement is pretty from a pretty vigorous.

And, so that is how these are the inclusions which are very very easy to identify and also they are the ones the easiest to take the micro thermo metric measurements and as I suggested when we started freezing operation we first take the runs on these particularly inclusions because we would only need to take two parameters T m CO2 and T h CO2 and these inclusions need not have to be relocated back for taking any other measurement.

And, even when we have other inclusions like aqueous y phase inclusions or the aqueous-carbonic inclusions and in the process of heating them even if these inclusions get destroyed which is chances are even low because they are very compressible liquid and their dp by dt slope is quite low. So, the chances of their decrepitation is also low.

So, only thing is that if we want to go for any in-situ or nondestructive analysis for this type of inclusions for example, we want to take a Raman spectra then this could be done prior to the microthermometric study or the suggestion would be that to take the character to subject them to such kind of long destructive in-situ analytical technique before attempting microthermometry. And the, if you remember we when we plan our microthermometry we break the wafer into workable size chips in which we can look for inclusions much more easily relocating inclusions easily.

So, I just standard practice if we are separate if we are disintegrating the fusion inclusion section to a number of such chips it is not necessary that all of them have to be subjected to micro thermometric experiments, some of them could always be preserved for such kind of in situ nondestructive analytical work.

These are some of the practical tips. So, density and isochore tricky for the methane bearing inclusions because any concentration any content of methane will decrease their density, but if you do not considered the concentration of methane then we will end up with overestimating the density of the carbonic fluid and the density and isochores are tricky forward methane bearing inclusions and they need to have a proper equation of state.

I only have given you an example that how possibly it could be done that by refining the parameters is the pressure correction in a in a modified relief on the question the a and b parameter could be also fitted for a mixture of carbon dioxide and methane with these parameters the volume correction parameter is b or save the non ideal parameters a and b parameters have to be available for the methane. And, sometimes these inclusions also do contents from H 2 S nitrogen or argon and those if available such kind of systems would also sub such compositions when they are detected the density also appropriately should be calculated using the equations of state.

The thermobarometry of these equations are reliable with intersecting isochore method and when we actually establish the coevality which itself is also a tricky affair and establishing coevality is mandatory.

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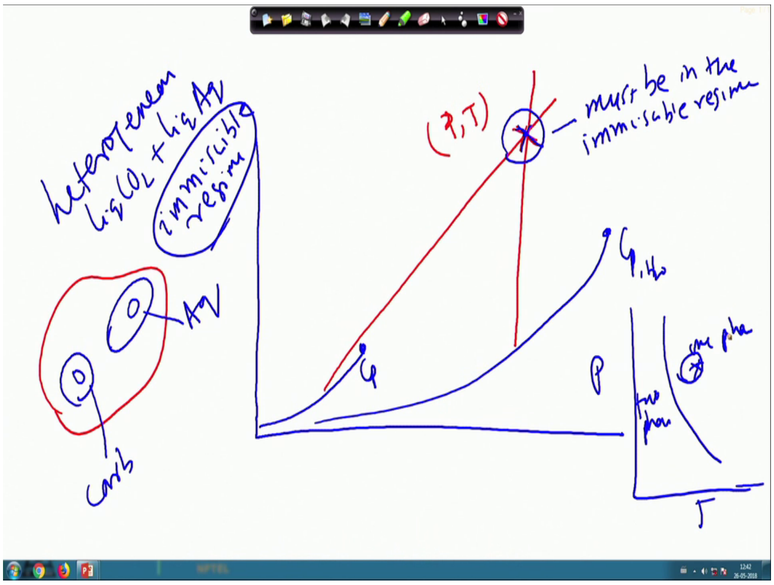

And, only one note of caution when were applying the intersecting isochore method is that say the diagram that we drew the cp of carbon dioxide this is cp of water or any brine containing known weight percent of NaCl and we are we are constructing the isochores. So, this is the isochore for the aqueous inclusion and this is the isochore for the carbonic inclusion.

Now, we know that they will be intersecting at a temperature and pressure at a point giving us a unique value of pressure and temperature. So, the note of caution here is that if we have done the thermo barometry on the coeval inclusion. This is a carbonic inclusion and this is an aqueous inclusion and we infer essentially that at the time of entrapment the fluid was heterogeneous a combination of liquid carbon dioxide and liquid aqueous. So, that means, we are actually in the immiscible resign.

So, if we are obtaining a pressure and temperature value by intercepting isochore method by using coeval pure equation pure carbonic inclusion this pity value also should strictly correspond to immiscible resign. Any value of pressure and temperature that we are getting and because we know that if we put it on a pressure temperature a region in the diagram, so, we know that this is pressure and temperature if we are considering to be some kind of a bulk if we reconstruct a bulk XCO 2 and the weight percent initial in the carbon in the water it will of course, be not that that very and easy and exercise.

So, we actually, our interpret was we considered that the fluid was in the two phase region and this is the one phase region. So, if it so happens that the pressure and temperature value that we determining here is falling somewhere here. Then, in that case it is a an explanation has to be found out or in that case it will be suspected that possibly there is something wrong; that means, either we are not talk we are not they are not coeval or there has been some amount of post entrapment compositional change. Or that these two fluids that we are seeing as a carbonic component and then aqueous component possibly came from different sources and what we saw them, adjust as a at the coincidence that they were existing as immiscible fluids, but actually we were immiscible in a move your in one phase design.

So, the only note of caution to be of adopted here is any pressure temperature estimation that we do by intersecting isochore method and those pressure temperature value has to be checked for the, for their consistency with respect to the immiscible resign. And, then aqueous-carbonic inclusions are the most difficult ones on account of the uncertainty in the recording of the temperature of melting of clathrate as we have discussed, you say colorless solid and its formation within the ice that is formed in the aqueous component is sometimes not very noticeable.

But as I as they practical tip that I offered that it is basically the diffused boundary or the meniscus between the two liquid that is a aqueous liquid and the carbonic liquid and the temperature at which the meniscus becomes very clear and the preferable covering preferable starts moving inside the carbonic liquid component liquid area that gives us the a surest indication of melting of the clathrate and, but that has to be reproducible.

And, the one of another important problem with these aqueous-carbonic inclusions is that most such inclusions data cannot be recorded and cannot be used because of the very simple fact that the most of them the larger ones eventually will decrepretate before total homogenization. That means, when we do the experiment I increase the temperature to a certain extent they suddenly we find that the inclusion decrepretatedly leaked.

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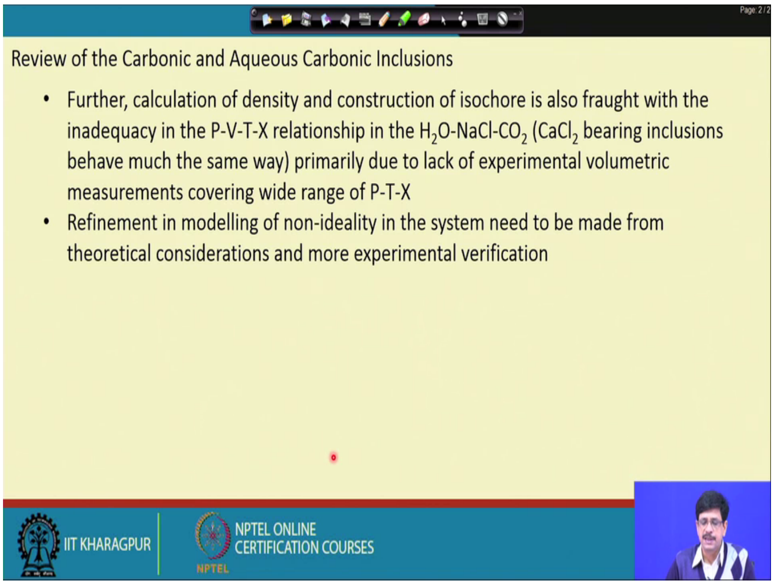

Review of the Carbonic and Aqueous Carbonic Inclusions

- Further, calculation of density and construction of isochore is also fraught with the inadequacy in the P-V-T-X relationship in the H_2O-NaCl-CO_2 ($CaCl_2$ bearing inclusions behave much the same way) primarily due to lack of experimental volumetric measurements covering wide range of P-T-X
- Refinement in modelling of non-ideality in the system need to be made from theoretical considerations and more experimental verification

The calculation of density and the construction of isochore and in case of the aqueous-carbonic inclusions is also quite I mean it for it is fraught with the inadequacy in the P-V-T-X relationships which still needs for the refinement and is still people are attempting to do that using many theoretical consider it seems. Like these days the molecular dynamic simulation has come to as one of the important reliable tool in reproducing P-V-T-X relationships in fluid mixer and sometimes also they fluid could also have calcium chloride, but what is been observed the behavior of the inclusions do not change drastically much from a pure NaCl H 2 O CO 2 or if it contents NaCl incase CaCl 2 H 2 and CO 2.

And, so, this uncertainty in the density of the isochore is primarily due to the lack of experimental volumetric measurements covering larger ranges of these values means. We do not have a full range of experimental data available, had it been available possibly it could have been much easier to calculate the density and the isochore. And so, the refinement in modeling of the non ideality of the system is still in it is for the refinement and the theoretical considerations and more of experimental verification.

So, with this we conclude our discussion on the fluid inclusion types, whatever basics we could discuss about the petrography, establishing the temp time relationship between entrapment of different types of inclusions in relation to the growth of the host mineral, primary growth or the recrystallization at any later time and identifying them making a proper planning of the micro thermometric experiments.

And, then have browse through kind of the responses of the different types of inclusions like the aqueous biphase, aqueous polyphase pure carbonic and the aqueous-carbonic these are the broadly the dominant types that if you look at literature where or any book or literature where you see descriptions of the inclusions you will find. These are the dominant ones which are described and also sometimes the exotic ones like once with containing graphite daughter crystal or inclusions which just so very briny that they contain more than even up to 10 daughter crystals or sometimes daughter crystals of hematite and sometimes even a flake of some micro sis mineral occurring is a daughter crystal. Well, whether it is actually daughter crystal or a captive crystal needs to be a certain.

So, other than those once the most dominant commonly occurring ones are these 4 the aqueous biphase, aqueous poly phase, the pure carbonic and the aqueous-carbonic ones and then we have also you one of the import thing is that when we sit down to present the data we also do use the same type of histograms for presentation of data on the. So, we have done in measurement on a lot of inclusions carbon pure carbonic inclusions. We would also like to present in the form of histogram to see how is the distribution in terms of because we if we get a depression from the of the on the freezing point value from minus 56.6 to going to many to a much lower temperature also present them as histograms of the density as well as the temperature of melting y’s and temperature of homogenization of the carbonic component.

What we generally cannot do is there is no other way, but we will discuss that how when we go to specific case studies and whether the fluid evolution diagrams that we present in case of the aqueous biphase inclusion that the or the aqueous inclusions only could also be looked at in combination with the results that that we obtained from the carbonic inclusions. Because, they also do also do substances they represent a substantial part of the fluid characteristic in terms of the temperature and composition and they are in integral part of the evolution of the fluid in any crustal domain.

So, we will see them as much as we can through the case studies on or the application to the mineral to the fluid inclusions to different types of situations to ore forming environment to metamorphic deformation and so on. So, hope to continue in the next class, to on the will begin with the application of the fluid inclusion results.

Thank you, so much.