Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application

Prof. M K Panigri
Department of Geology and Geophysics
Indian Institute Of Technology, Kharagpur

Lecture- 11
Aqueous Fluid Inclusions

Welcome to today’s lecture during the last 2 weeks we have been discussing about the fundamental aspects. And at this point of time we possibly can correlate the occurrence of fluid inclusions in host minerals.

And the on the basis of the pressure and temperature condition of their entrapment and also the post entrapment phase changes that, we see in the inclusion as occurring combination of different phases like liquid plus vapor or liquid plus vapor plus a solid. And we can correlate the such occurrences to the condition of the entrapment.

As well as the chemistry of the gross chemistry of the fluid in terms of whether it is a pure water or it is a water plus salt or water plus salt plus gas. And the with our basic assumption that the entrapment was homogeneous, entrapment condition was homogeneous and the inclusion behaves as a close system and follows an isochoric path after its entrapment in the host mineral.

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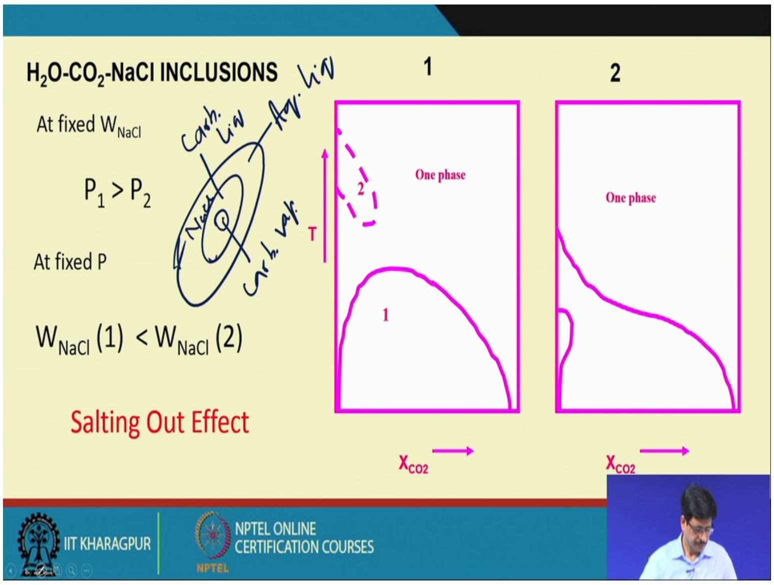

H_2O-CO_2-NaCl INCLUSIONS

At fixed W_{NaCl}

$P_1 > P_2$

At fixed P

$W_{NaCl}(1) < W_{NaCl}(2)$

Salting Out Effect

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I would just like to add a little bit of a little bit of component to the basic understanding of the principles of microthermometry so that we can correlate the occurrence of the inclusions.

And as you as has been told in many instances the inclusion that we see dominantly the aqueous biphase occurring is liquid plus vapor or aqueous polyphase with occurrence of put it in a very simple way a salt crystal; may be of a sodium chloride, which is dotted crystal that precipitate from the inclusion fluid after its entrapment.

Or it could be a situation in which an inclusion can have an aqueous liquid, a carbonic liquid and a carbonic vapor, which can be explained on the basis of a binary phase relationship between water and carbon dioxide. As we all know that the water the aqueous component is also never a pure. A aqueous component will invariably have dissolved solid in it and in and in most cases the dominant solid is sodium chloride.

So, the aqueous carbonic inclusions which we see has the aqueous liquid part on the carbonic part; that means, we know that the inclusion which is occurring which is occurring; like in here it is an inclusion it is the aqueous liquid, this is the carbonic liquid and this is the carbonic vapor. We know that this aqueous liquid will have the dissolved solid in it and in most cases it will be dominated by NaCl.

And so that so, that is the reason why a ternary system like this H 2 O NaCl and CO 2 can be invoked to understand or to understand the situation in which an aqueous carbonic inclusion will occur.

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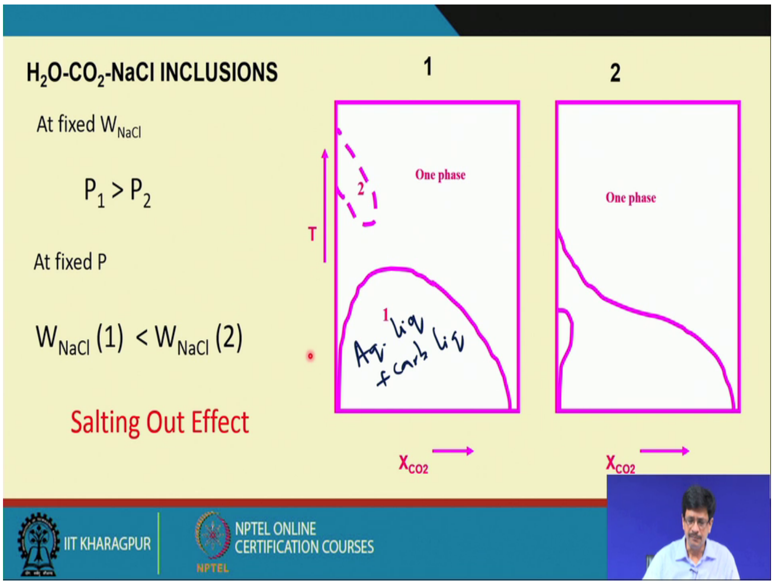

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Salting Out Effect

And this system that is the reason why it is one of the most studied system with of course, we know that there could be other dissolved solids other chloride species. But they can be always be approximated to belonging to this simple ternary, which is carbon dioxide water and NaCl. Although it look simple, but this is the system in which a lot of work has been done with limited experimental data available from which some understanding can be made in terms of the entrapment of inclusions.

So, what we see here it is all it sometimes becomes easier to represent the ternary in terms of a the binary or assume a binary. We can always think of that this is a like the binary which we consider before is water and carbon dioxide. We can say that this water also has fixed concentration of the electrolytes like sodium chloride in terms of weight percent which can be expressed.

So, these 2 diagrams which have been shown here represents the some such kind of pseudo binary explaining the conditions in which there will be a one phase fluid and the situation pertaining to where the fluid will be splited up into 2 different phases as an aqueous liquid plus carbonic liquid.

So, if you look at it very simplistically; so, diagram 1 and diagram 2; and diagram 1 we see that we see the solve solvers as we saw before an asymmetric solvers and a critical point will be somewhere here. And so, this represents the condition in which it will be 2 phase situation and aqueous liquid plus a carbonic liquid and it will be one phase.

What we see here that there is also a reason of invisibility, there is also in region of invisibility which is being generated in a ternary system. And on the second diagram we see that this region of invisibility is further expanded and it is become a continuous area in which it is a 2 phase situation.

So, situation 1; if we consider that they are at fixed weight percent in a say let us say 6 weight percent sodium chloride in the aqueous phase. Then if you are considering these 2 diagram to representing fixed weight percent NaCl, then the pressure in case one has to be greater than in case of a diagram 2. Because the solubility of carbon dioxide in water is a function of pressure; so, with a fixed weight percent sodium chloride more amount of carbon dioxide could be dissolved and that is the reason why the invisibility field is little less compared to the figure 2.

Now, if I consider the pressure to be fixed corresponding to one single pressure value; then the weight percent NaCl in case of one would be less than that in case of 2. So, that gives us an idea that if with a fixed consideration of water and carbon dioxide; if we increase the sodium chloride content then the invisibility also will increase invisible area. So, this is something which is very popularly (Refer Time: 08:05) well known in basic chemistry knowledge.

This is salting out effect that if we have some amount of salt dissolved in water and we try to dissolve a non electrolyte carbon dioxide, then the concentration of the salt will fall on it the salt will get out of the system or it is basically something, which you can call as a salting out effect.

So, this much of addition; so this is going to explain; so, we can think of the our homogeneous one phase water plus carbon dioxide plus salt fluid which is a supercritical fluid or could be in its liquid filled depending on the pressure temperature that we are considering. So, this the inclusion can be trapped in the host mineral anywhere in this one phase condition and as the temperature decreases, its split splits up into 2 and we see them occurring as mixed aqueous carbonic inclusion; with salt being present in the aqueous component.

And invariably the solubility of the electrolyte like salt like sodium chloride will be very negligible in the liquid carbon dioxide. So, it is aqueous component which will be accommodating the salt that is there in the system after the splitting or after the post entrapment phase separation. So that will somehow that gives us the theoretical the framework on which we can understand the entrapment process and we correlate the physicochemical the physical parameters like pressure temperature and also composition and the post entrapment phase separation process.

So, with this we will now move on to on to understand the thermal response; the response of inclusions to heating freezing cycle and we will start with the simple system of water plus sodium chloride.

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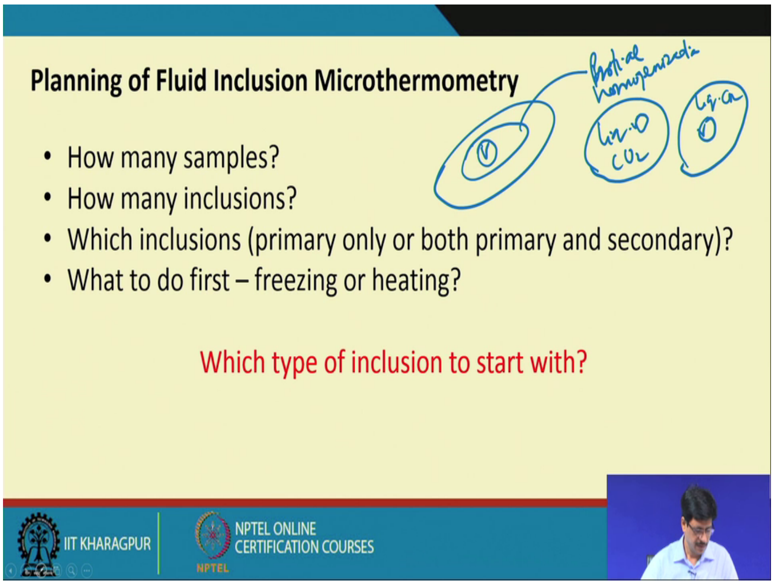

Planning of Fluid Inclusion Microthermometry

- How many samples?
- How many inclusions?
- Which inclusions (primary only or both primary and secondary)?
- What to do first – freezing or heating?

Which type of inclusion to start with?

So, before that we would also like to add a little bit to the questions that we posed during the concluding part of the last weeks lecture; that how many samples we said that well the depending on the nature of the research problem nature of the exactly the what we are trying to address, depending on different geological environment.

It is not a very fixed value that we need to need to study 100 or 1000 or 5 or 10 samples and how many inclusion? This also as this particular methodology is very much dependent on the quantum of data, so the more the better and here which inclusions that the inclusion, which you whether we would go for the primary at the primary of the secondary both is also depends on the nature of the problem that we are addressing.

And what we should do first and the answer was that will be doing freezing. We will explain we will elaborate on this point that what will happen if we start heating the samples and try to do homogeneous in experiments through some illustrations. But there is one question which possibly will come into the mind of the beginners that which type of inclusions to start with when we begin our microthermometric experiments.

Out of the types of inclusion that we have discussed so, far the inclusion which are the pure carbonic inclusions; an inclusion which is occurring as a pure carbonic inclusion where only it is a carbonic either its a monophase or in the form of a biphase. This is liquid CO 2, this also liquid CO 2 and this is the vapor.

So, these inclusions are essentially the easiest one to do the microthermometry and because we just need to if the if there are pure carbon dioxide or even if this particular liquid carbon dioxide is charged with the variable concentration of methane. Then we know that we have to in order to obtain a homogeneous condition for this particular inclusion. In order to obtain a homogeneous state for this particular inclusion we may have to just heat it only up to 31.1 and that is the critical temperature of carbon dioxide.

And if if it happens to contain some amount of methane the critical temperature will be in less and if it is not a critical homogenization, then we can get the homogenization temperature anywhere below from minus 56.6 to plus 31.1. So, the sample is not being subjected to any higher temperature and you also know that if the inclusion is a monophase liquid carbonic inclusion, then by decreasing the temperature by a few degree from room temperature, the vapor phase will nucleate and we need to just determine at what temperature this particular vapor phase nucleated and or vice versa the exactly the temperature at which the homogenization is taking place.

So, in a way I would suggest that when we begin our microthermometric experiments after doing routine petrography and we have got the fluid inclusion (Refer Time: 13:39) fluid inclusion section. And fragmented into different chips well leveling them in terms of the occurrence of the inclusions; what type of inclusion in which area of the fluid inclusion section.

And then put the first chip into the stage if the one of the inclusion types to be there in the fluid inclusion section happened to be the pure carbonic inclusion, it is always easy a better to start with them. Because another important reason that we did not have to relocate them for any further analysis. Because we have got their homogenization condition and then we can begin our freezing experiments with other type of inclusion; let us say the aqueous biphase inclusions are the aqueous carbonic inclusions.

And even the aqueous carbonic inclusions also can be frozen can be subjected to freezing experiment first where the where we know that the liquid carbonic component also will have a with a vapor. And we can we also can get a partial homogenization of this carbonic component which will come to partial.

Exactly as it happens in a pure carbonic inclusion, we also can get it get the homogenization of the carbonic liquid part, if the vapor is present it will also homogenize to a to either a liquid or vapor. So, this we will illustrate through our examples.

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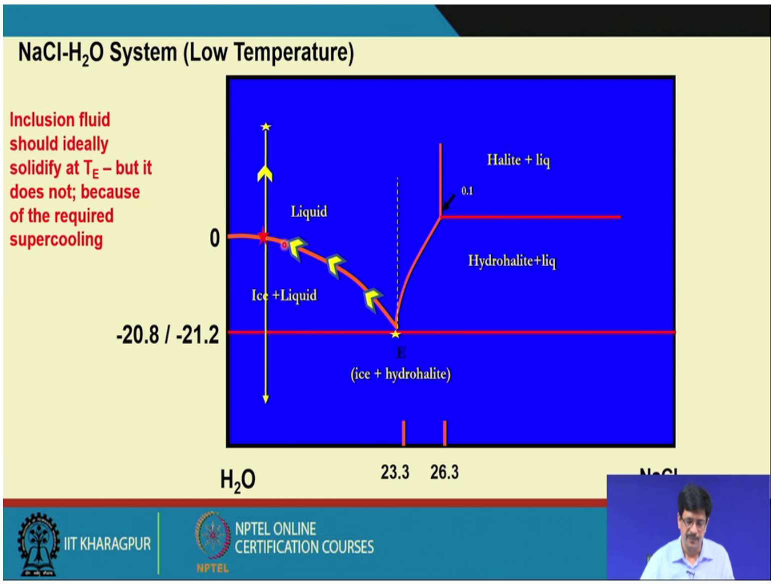

NaCl-H_2O System (Low Temperature)

Inclusion fluid should ideally solidify at T_E – but it does not; because of the required supercooling

Ok. So, now, we move on to the response of aqueous biphase inclusion to heating freezing experiment and will start with freezing first. This is diagram which you have already discussed is a binary water NaCl diagram and this is only up to limited compositional range.

So, beyond which we know that it will be an inclusion, where they will be solid halide sodium chloride present along with water. And the such inclusions which are aqueous polyphase inclusions containing a liquid plus vapor plus sodium chloride as a dotted crystal are generally not subjected to freezing experiment. Because of the fact that we know already that the liquid is already having the saturate the value of room temperature saturation with respect to sodium chloride.

And the bulk composition in terms of the sodium chloride content of the total inclusion cannot be determined only by doing the freezing and which we will discuss later. So, as far as the inclusion which have the sodium chloride weight percent equivalent up to room temperature solubility; means those inclusions which will not have any dotted crystal of sodium chloride in them, they can be subjected to freezing experiments.

And if they happen to be on the water rich side; let us say that this star is representing a composition which is on the water rich side. And we will see the, what is we are going to freeze this particular inclusion; that means, the temperature is decreased in the in the apparatus by using liquid nitrogen.

And theoretically when this inclusion is being frozen has been subjected to lower temperature, ice should start forming should form as and when the temperature is the cotectic temperature ice plus liquid coexistence; cotectic temperature is reached. But eventually we will see that the ice is not ice will not form at this particular temperature; we need to decrease the temperature for below then corresponding to the temperature of it at which the ice is expected to form or the temperature you take it.

This is a phenomena which we know it is a which is known by a phenomena call supercooling that is many a times required. And there is no fixed value that how much of degree of supercooling will be required for a particular inclusion; it could be pretty variable. For example, if the inclusion is a pure water plus sodium chloride liquid and the eutectic temperature corresponds to minus 21.2; we may need to freeze it to minus 40 minus 50 or minus 60; it is quite variable and different inclusions maybe need different degree of supercooling to form the solid.

So, once the temperature; the temperature the because the temperature has been decreased to a great extent and the inclusion becomes frozen becomes totally the content of the inclusion cavities solidified. Then it actually will be a situation from where if this is far below; the temperature eutectic then what exactly is done is by reversing the process and by slowly warming up that frozen inclusion to gradual higher temperature.

So, we know with increasing the temperature from value far below the; that of corresponding to eutectic, we will be reaching the temperature eventually we will be reaching the temperature corresponding to the eutectic. So, once we reach the temperature corresponding to eutectic; so we apply our basic knowledge of phase relation. Here in this eutectic corresponds to 2 solids, that is ice plus hydrohalite. Hydrohalite is basically sodium chloride and 2 molecules of water and say NaCl to H 2 O. And at this point of time; if we put the temperature on hold at the eutectic temperature the hydrohalite will melt out.

So the hydrohalite will melt out and now it will enter into the ice plus liquid cotectic. We are warming the inclusion gradually from its sub 0 temperature temperature corresponding to minus 21.2 and then finally, the ice will melt here. So, essentially the freezing experiments that we do on this inclusions are essentially in a; the recording of the phase changes are better than on a reverse route rather than on the director and because that the fact that it will need to be supercooled.

So, determining the temperature of formation of ice cannot be recorded; it will only be recorded in the terms of the melting of the ice. For example, when we are increasing the temperature, it goes it moves on the cotectic and reaches the point exactly where it would have intersected the cotectic and here we are solid will melt and they solid only ice.

Because this on this cotectic it is a ice plus liquid equilibrium ice plus ice plus liquid coexistence situation. And we can still further even if we heat bring the inclusion to the original ; suppose this corresponds to a room temperature, it will always be a good practice to bring it to room temperature or even we can just record because here only the temperature that we need to record here is this temperature.

So, it is essentially will be the temperature will be the depression in freezing point this point corresponds to depression in the freezing point because 0 is here and its a non-linear curve, you can see here. So, this will be; so, depending on as you can make out from 0 always pure water coming to the eutectic composition of 23.3 percent NaCl any bulk composition, we think in this area either here or here or here. So, their depression will be more for a pure from 0 degree centigrade corresponding to the melting the pure water pure ice.

So, our objective is to estimate the salinity of this particular biphase inclusion and express it in terms of weight percent NaCl equivalent. And there is one many experiments done by many people many different laboratories where the depression in freezing point with variable sodium chloride concentration has been measured. And since this happens to be nonleanear curve, it can be approximated to an equation.

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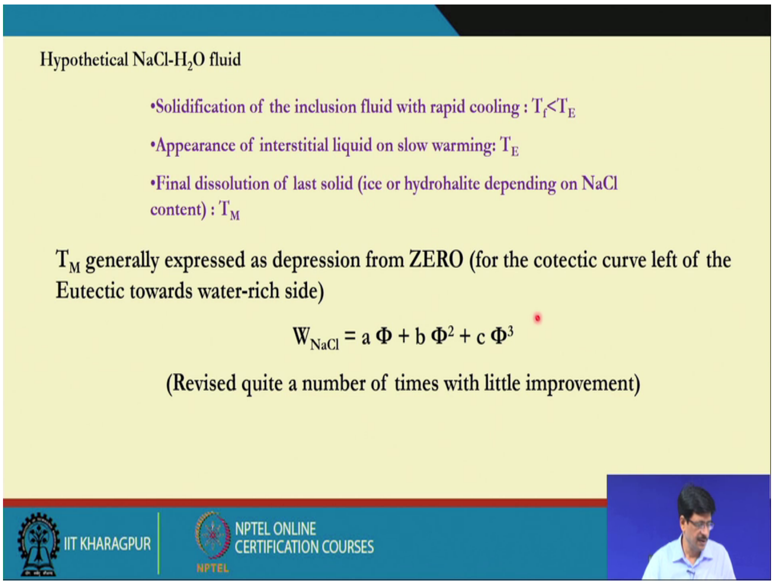

Hypothetical NaCl-H_2O fluid

- Solidification of the inclusion fluid with rapid cooling : $T_f<T_E$
- Appearance of interstitial liquid on slow warming: T_E
- Final dissolution of last solid (ice or hydrohalite depending on NaCl content) : T_M

T_M generally expressed as depression from ZERO (for the cotectic curve left of the Eutectic towards water-rich side)

$$W_{NaCl} = a\,\Phi + b\,\Phi^2 + c\,\Phi^3$$

(Revised quite a number of times with little improvement)

So, in a hypothetical NaCl is to fluid; the solidification of the inclusion fluid will be rapid with rapid cooling the freeze temperature at which it will I; it will completely frozen which you can represent is T f will be much less than that of T E corresponding to eutectic temperature in the binary.

And now the interesting situation which will also be discussing here, we will start that temperature corresponding to eutectic will also be a characterized by formation of interstitial liquid in the inclusion which was frozen.

So, that is a appearance of interstitial liquid that actually will be help us in knowing what is eutectic temperature. And the final dissolution of the last solid that is ice or hydrohalite depending on the NaCl content that will be recorded is T M or even sometimes people designated a T M ice.

We will a list out the abbreviations of the notation that we use in our microthermometric experiments. So, this T M generally is expressed as a depression from 0 for the eutectic curve left of the eutectic towards the water rich side means this part. And it suppose it is approximated to a third degree polynomial as alpha phi beta phi square and ceta phi c phi cube.

So, here a b and c are coefficient, which have been worked out and phi is the depression of freezing point from 0 expressed as positive quantity. Means in if it happens to be minus phi it will be phi or minus 10 will be 10. And these equations has been revised n number of times and are given this coefficient and the value for depression in freezing point one can always calculate the salinity.

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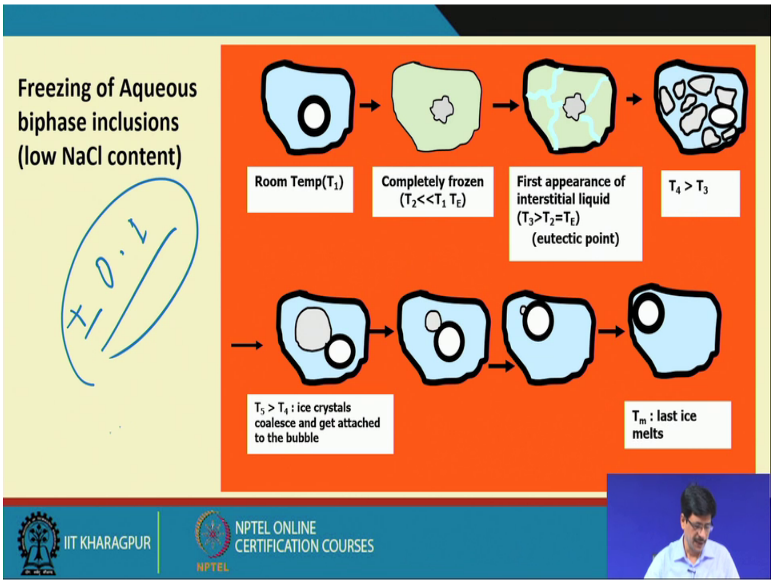

Freezing of Aqueous biphase inclusions (low NaCl content)

± 0.1

Room Temp(T_1)

Completely frozen ($T_2 << T_1\ T_E$)

First appearance of interstitial liquid ($T_3 > T_2 = T_E$) (eutectic point)

$T_4 > T_3$

$T_5 > T_4$: ice crystals coalesce and get attached to the bubble

T_m : last ice melts

So, here it just this sketch is exactly to even though it will be much easier to see them in a video of exactly inclusion undergoing freezing which one can always see, but this sketch we give sort of ideas to what exactly happens.

So, this is our original room temperature aqueous biphase inclusion is the liquid, this is a vapor. And now this corresponds to the temperature of freezing the T f, which is after a substantial supercooling and the inclusion will be completely frozen. Remembering the fact from a basic phase diagram unary water where water has the unique property of increasing in volume on becomes on solidification.

So, this particular liquid on becoming solidified will undergo expansion that will cause the vapor to shrink in its volume because vapor is compressible. So, the vapor for vapor will vapor bubble will shrink and become deformed. Now this corresponds to temperature of the eutectic temperature and you could see that what is marked with this kind of curved line; thick line is essentially the interstitial liquid.

This corresponds to temperature of the eutectic temperature where the this liquid is actual formed by melting of the hydrohalite solid. So, now a situation is here that we have ice plus liquid and the hydrohalite just melt, you can hold the temperature there; we can still reproduce it and that is the temperature the eutectic temperature in NaCl is to system.

So, first appearance of (Refer Time: 26:04) liquid. So, what we need to do? Optically we have to get ourselves accustomed to see how they look or the how the optical property of this in frozen inclusion changing. Because in this case here there will be a good refractive index contrast between the solid, which will be ice and the liquid which will be sodium chloride rich.

Now if we take an intermediate temperature somewhere on the cotectic corresponding to this anywhere on this. It will be represented by this diagram where we will see the bubble. Now the bubble has a come back to its original size, but not necessary this spherical shape and we will have this ice crystals actually flooding inside the inclusion cavity in the water gradually the more and more ice is melting.

And the water here is becoming more and more diluted with respect to sodium chloride and this solid ice is got a very unique property. As you can see here that there is a initially to start with we might see some multiple such fragments of this ice and that all these ice will coalesce to form one mass of ice with a circular outline. And with further increase in temperature on the cotectic the ice will become smaller and smaller in size.

And in addition the size is also got a unique property that it will get attached to the bubble. And it remains it remains attached to the bubble till it finally, disappears and it comes backs to the original compare you can very well compare; this was original inclusion again after the melting of the inclusion it is exactly the same that you have come back.

And because the ice is attached to the bubble; so, during the melting of the last ice; the bubble undergoes a movement. Sometimes it becomes a rapid movement deform of a jack can, which helps us in actually determining precisely recording the temperature of last ice melting. Now here there could be many practical thing which could be discussed that what kind of rate of may cooling rate of warming up that we could; we should be doing for to be good practice.

As we know that our heating freezing systems that were using can be can have a variation from almost like 0.1 degrees per minute to even 100 degrees per minute kind of rate and we know that one and essentially in any kind of recording of the microthermometric parameters for this kind of inclusions; they need to be the section when need to be repeated the replicated and the value. Say for example; in this case suppose the ice is melted at minus 2.0.

So, we need to reproduce it to plus minus 0.1; we would say that in case of if the we need to replace reproduce the freezing blast melting temperature of ice to plus minus 0.1 and that will would be will as acceptable. So, do in order to do that the rate at which will be warming, when the ice has started to melt or as ice has decrease in a size considerable; the less will be the less is the warming rate the better it is or the better is the possibility that will be able to reproduce the value exactly. So, it is; so these are the practice sometimes we know that inclusion will become totally completely frozen that minus 60.

So, from room temperature to minus 60 we can go at a faster cooling rate, but we have to again have a very control warming rate when the temperature eutectic could be reaching. So, that we know that would be able to record the exact temperature eutectic without introducing much of error even though these are all they only come after practice.

And this one is just the extension or the considering the binary in a region where it is sodium chloride reach beyond the eutectic composition; if the composition is somewhere here. The similar thing will exactly happened we have to supercool it too much lower temperature than eutectic. And so, here the behavior will be little different that up to the point of T E whatever we have discussed will hold good.

But here now corresponding to temperature, where it is above just below the temperature of last ice melting, we will get because on this particular cotectic we will have liquid I will have ice plus hydro, but the situation corresponding to here when the concentration they composition is a higher sodium chloride content, then the eutectic composition.

Then at new eutectic temperature all the ice will melt and this is corresponding to that kind of a situation. And on further warming all the ice will melt and the solution will become more and more and each with respect to hydrohalite. And the last solid which will be melting will be hydrohalite in place of ice as it since it is a sodium chloride, which part of the binary. So, the last solid, it will be melting is hydrohalite; so, it has been I have described in a little exaggerated manner; the hydrohalite crystals will be optical different as you can see here that we clear cut difference in the refractive index between hydrohalite and ice.

Hydrohalite will also do not have the, we will not have the tendency to coalesce to form one single crystal; they will be there also then do not get attached to the vapor bubble. And it becomes it will not that very difficult for an experienced the fluid inclusion user to understand the whether the last ice last solid that is melting whether it is ice for hydrolite.

So, in this condition compared to the situation, where its water rich side; the sodium chloride rich side will have hydrohalite is the last solid to be melting.

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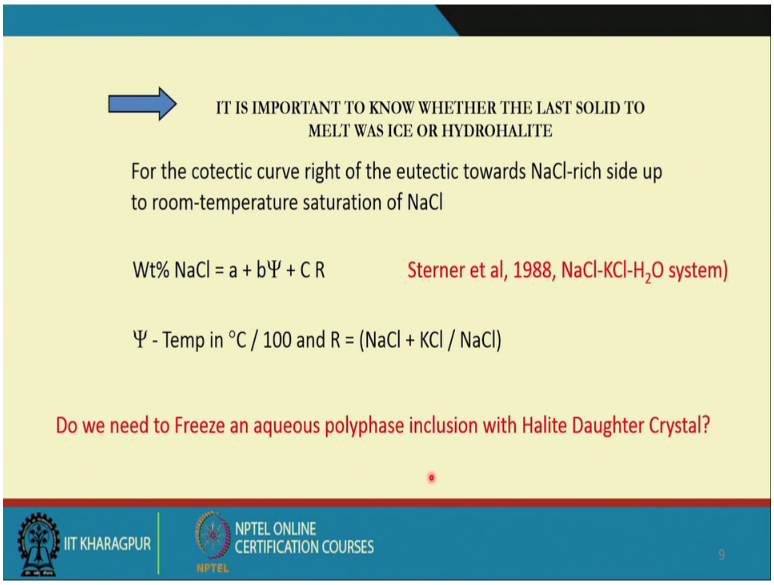

IT IS IMPORTANT TO KNOW WHETHER THE LAST SOLID TO MELT WAS ICE OR HYDROHALITE

For the cotectic curve right of the eutectic towards NaCl-rich side up to room-temperature saturation of NaCl

Wt% NaCl = a + bΨ + C R   Sterner et al, 1988, NaCl-KCl-H_2O system)

Ψ - Temp in °C / 100 and R = (NaCl + KCl / NaCl)

Do we need to Freeze an aqueous polyphase inclusion with Halite Daughter Crystal?

So, that also in that case also when one can calculate the weight percent NaCl equivalent. And by equations, which has been like this simple equation where they R corresponds to because it was worked out in a ternary system NaCl, KCL and water.

And with known parameter of a and b, where this sized temperature in degree centigrade divided by 100 one can calculate the weight percent if it is a sodium chloride reach. As I have said that if we have a situation corresponding to a polyphase inclusion, a water plus water liquid water plus vapor plus sodium chloride crystal; then if is that will only be able to see the melting of the hydrohalide and the last are the solid crystal will keep on persisting to higher temperature.

So, this inclusions which a polyphase inclusion containing halite dotted crystal; there need not be subjected to freezing experiment and what to do about them will be discussing an our subsequent lecture. So, we conclude the today’s discussion on the response of the aqueous biphase inclusion to microthermometric experiments and mainly its freezing. So, we will continue in the next class.

Thank you.