Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application
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Lecture – 08
Microthermometry: Principles (Contd.)

Welcome to today's lecture on Fluid Inclusions in Minerals. We have been discussing about the micro thermometry, the basic the principles. We have micro thermometry of fluid inclusions and starting with the very simple in case of the aqueous inclusions being trapped in the homogenous condition could be either in the liquid field or in the vapor field.

And we will discuss about the situations in which the fluid will be in homogenous and what will be the situation and what will be the nature of fluid inclusions and what will the indicate in the subsequent classes.

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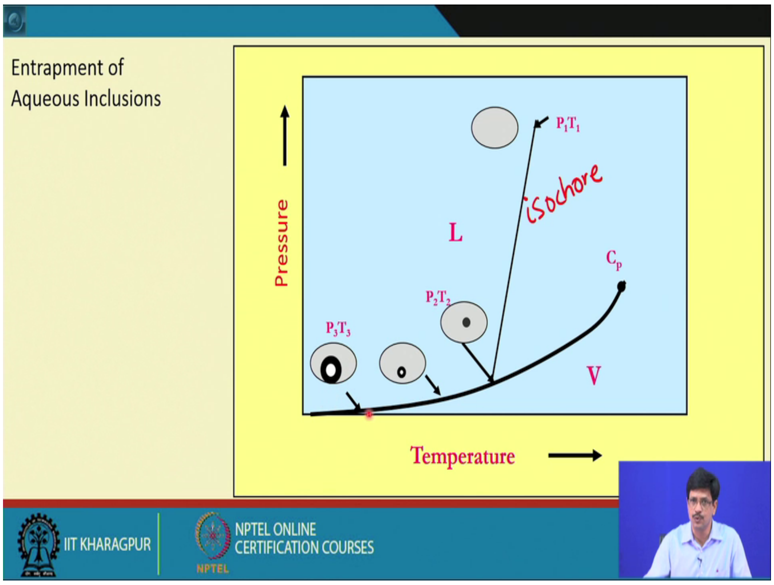

So, we will just; so, in continuation of what we were discussing in the previous class, we will try to pressurized the entrapment of aqueous inclusions, and the post entrapment phase change that we observe in them and the way we see them in the in room temperature as a combination of phases in heterogeneous condition, how it actually takes place? So, let us consider a condition corresponding to temperature and pressure P 1 and T 1 within the liquids liquid only stable field in the P T space.

I am only considering I am only showing the boiling curve here, because of the simple reason that any mineral forming process in the suppression condition happens at temperatures higher than at least 50 degree Celsius or in much more than that. Conditions corresponding to sub 0 or much lower temperature is not possible for minerals to grow. And, so we will consider the situations which are most common, and will talk about situations which are less common or exceptional later.

So, let us consider that here just at the shown at the arrow the, Emmanuel is growing here. Primarily precipitating from the fluid after it attains saturation, and let us say that the within that solid lattice of the mineral this packet of fluid, this cavity this fluid has been encapsulated. Now this is in a one phase condition.

As we as for our assumption, this particular fluid this particular inclusion will continue to remain in it is one phase condition, all through and will follow a constant density constant volume constant composition path which is the isochore. And now so, it will continue to move on this which you can say that it is the isochoric path. It will continue to move it may just immediately after the entrapment of the fluid or even a considerable time gap even in terms of millions of years or 100s of millions of years is generally the case.

So, is an when it moves along the isochoric follows the isochoric path, and it will continue to do. So, till the point that it intersects the boiling curve as shown on this arrow over here. So, as an when it intersects the boiling curve and reaches the point; let us say, that point corresponding to that is P 2 T 2 and write at this point here we observe that there is a post entrapment phase change that is taking place here, and a vapor bubble is a nucleating.

It is always much easier to understand with respect to this phase diagram. Or it also it can be explained on the basis that because the liquid has got a higher coefficient of thermal expansion then the host solid.

So, the liquid will contract faster than the host mineral and the vacuum that is created because of the differential contraction of this liquid the vapor phase will nucleate. But it will always be better or more easy to understand in this way that as an when it intersects the boiling curve, a vapor bubble nucleates because it is essential condition of coexistence of liquid and vapor. Now let us consider any other pressure temperature condition on this because any further decrease in the pressure at temperature will make it move only on the liquid vapor coexistence curve.

It cannot move away from the liquid vapor coexistence curve. Because any amount of other construction of this liquid will only make the vapor bubble to go larger in it is size. And let us talk about situation which is P 3 T 3 is corresponds to the temperature and pressure pressurize one atmosphere that we see in our laboratory, and the temperature is room temperature, and at which we see that this fluid or the originally trapped inclusion which was the homogenous inclusion is now observed as an inclusion with the liquid and a vapor bubble. And we know why this vapor bubble has got a darker boundary. And this right part is the central part of the vapor and this is the liquid.

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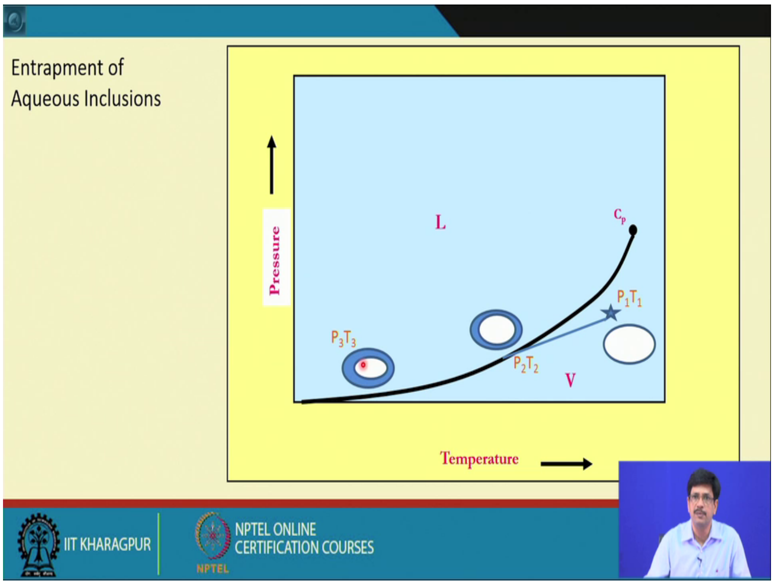

Now, similar situation can be visualized in case of a situation which is the vapor this is a vapor field. And let us say that the condition corresponding to this is P 1 T 1 in the vapor field, vapor stable field. And here the solid host is as a crystallizing or re crystallizing going over going or any kind of annealing process that is going on here. And this vapor is enrapt within the mineral solid lattice of the mineral. So, and this vapor because the densities of the vapor is usually very low.

So, it will always be a very so, shallow or a very low dP by dT slope. Yet, still it will on the way that further decrease in temperature and pressure condition. It will also going to eventually intersect the boiling curve at a at a point corresponding to P 2 T 2 as shown here.

So, as an when it intersects this vapor which is enrapt here as an when it intersects the boiling curve, a thin rim of liquid will appear or liquid will nucleate because essentially it is a condition corresponding to liquid and vapor coexistence. Similarly, as discussed before with further fall in the temperature pressure condition and till the time that we see them in the room temperature. We can only see that the liquid the content of the liquid or the proportion of the liquid has only marginally increase where it has been shown in a little exaggerated ways to make it more clear.

So, what happens here is that this originally trapped vapor on intersection with the boiling curve has given rise to a to nucleates or the liquid and finally, it is present is also is a liquid plus vapor combination. But the only difference between the case which was discussed on the previous diagram; here we get a vapor bubble which is proportionately much larger compared to the situation where the entrapment is form a liquid field.

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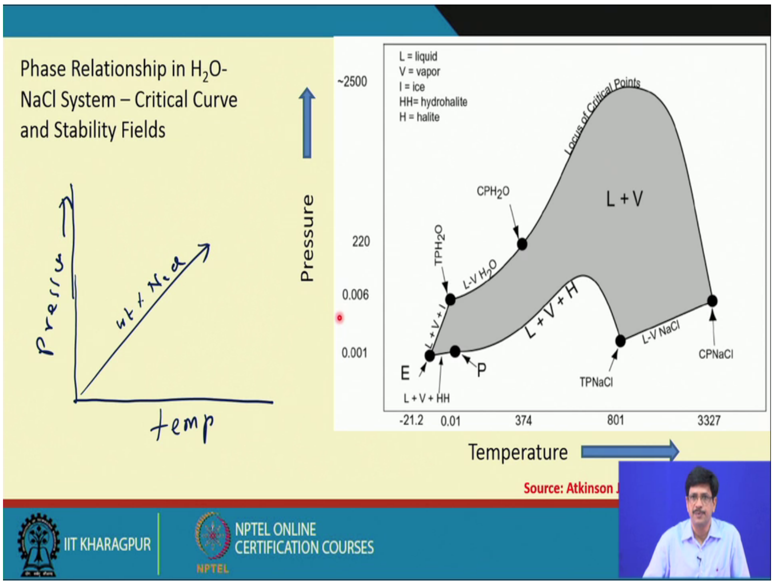

Since we have been talking about the situation that it is the water is never a pure water. The water is charged with dissolved electrolytes. And the electrolyte is dominantly in most of the cases is sodium chloride.

So, it would be worthwhile to look at this diagram which is a very simplified diagram essentially it could be the situation corresponding to if we involve, if we take the compositional variability. It should be a diagram on which you should be able to plot temperature, pressure and weight percent of NaCl or x NaCl or mol percent of NaCl whatever we might put in.

But then if you look at if we try to see the situation in the 3 dimensional diagram, it might become a little difficult for us to visualize. So, this diagram is in a way that it is kind of distorted. And what is been plotted here is we can is we can see here this temperature and pressure. And as you can I as you can identify this point is the triple point of water corresponding to temperature of 0 degree and pressure about 0.101 bar. And what we just show before the liquid vapor coexistence the boiling curve, culminating at it is critical point of water that is CPH 2 O, which is 374 degree Celsius and 218 bars.

So, as you know that as an as sodium chloride and water are soluble soluble in all proportions. So, the critical point of pure water, and here this point which is the critical point of sodium chloride is temperature of the order of 3300 degree Celsius.

So, they it is there likely to have to exhibit a continuous critical curve. And this critical curve; that means, if we take water pure water the critical point will be at 374 degrees Celsius 220 bars. And we all know from the colligative properties of solutions if we have this particular water having dissolved weight percent NaCl say 5 weight percent NaCl, then the critical the critical temperature is going to be elevated.

So, this curve black curve which is the locus of the critical points. So, that is how we see that the critical, the 2 critical points could be continuously join the situation coming from pure water to pure NaCl. That is what I was just telling that it could be a it could be better be plotted on a 3 dimensional excess on pressure temperature and composition. But for a better understanding we can always see look at this diagram.

Now the other part of the diagram if we look at this point which is marked as E which will discuss a little bit later. This corresponds to the freezing point depression of water, when sodium chloride is there corresponding to eutectic proportional of the mixture. And now since this particular point which is the triple point of pure NaCl means, where there will be liquid plus vapor plus solid NaCl coexisting, this point is marked over here.

So, this if you join in the point the eutectic temperature of liquid water and sodium chloride. And the triple point of sodium chloride, this will uniquely define this field where liquid plus vapor plus h is halite, halite is actually sodium chloride. So, this field will be the liquid plus vapor plus halite.

And the dark or the gray part so now, on this as we cross this particular line to higher temperature and pressure condition, the halite will not be stable here it will be liquid plus vapor field and this is the boiling curve. And this triple point of water which is 0 degree Celsius to the eutectic temperature of water will uniquely define the field and which a liquid plus vapor plus ice will be stable.

So, most of our micro thermometric measurements and the most of the calculations have to take into account, even though we do not need to understand the phase relations in from pure a water to pure NaCl; because most of our crystal fluids will be containing NaCl of the range of 30, 48 and 50, 60 percent of weight percent of NaCl. And while calculating the volumetric properties, because this is what one of the major one of the important exercise that fluid inclusion research involves.

In order to understand the behavior of fluid inclusions and the understand the micro thermometric data their interpretations, it is very essential that we understand the volumetric properties of this kind of mixed salt water systems. And what happens to the the volume as so this phase diagrams help us in understanding that.

So now, from the situation that we have been dealing so far is corresponding to the higher side higher temperature side, and the understanding the basic principles in terms of the entrapment because entrapment is essentially at higher temperature pressure condition.

From the conditions of entrapment, till the point of till the temperature and pressure conditions in which we are seeing them in the laboratory in a situation where it is not homogenous, but heterogeneous with a liquid plus vapor or liquid plus halite can be understood in this from this diagrams.

So, what actually possibly in these diagram in which you have shown, we only have talked about a an entrapment process which will be only resulting in a situation where it will be a combination of liquid plus vapor at room temperature. But we know that a situation also corresponds to that an inclusion is we can have an inclusion.

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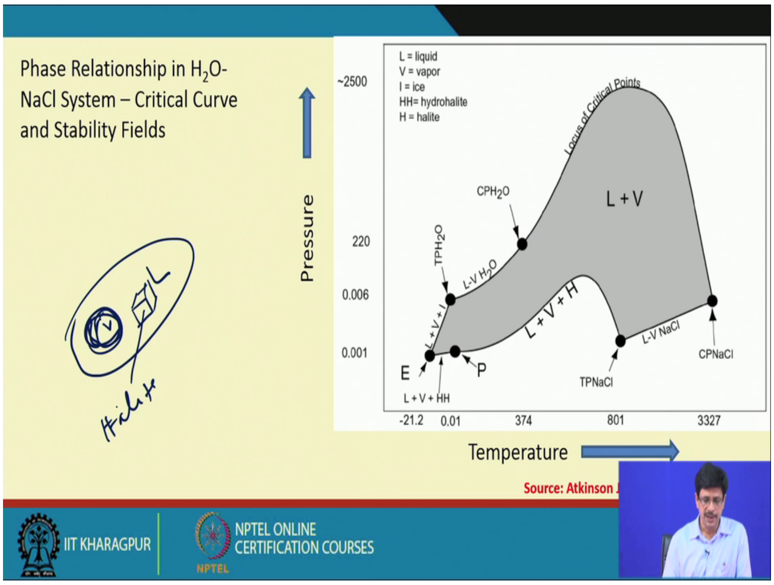

As we all know that there could be a vapor this is a liquid, this is a vapor and there could be a solid crystal and let us say this is the one halite. So, the condition which will be corresponding to that is only possible if we have during the time of entrapment even if I go back to this diagram if we consider this diagram, then with the help of this what we can say here; that this particular fluid which is getting enrapt corresponding to pressure and temperature.

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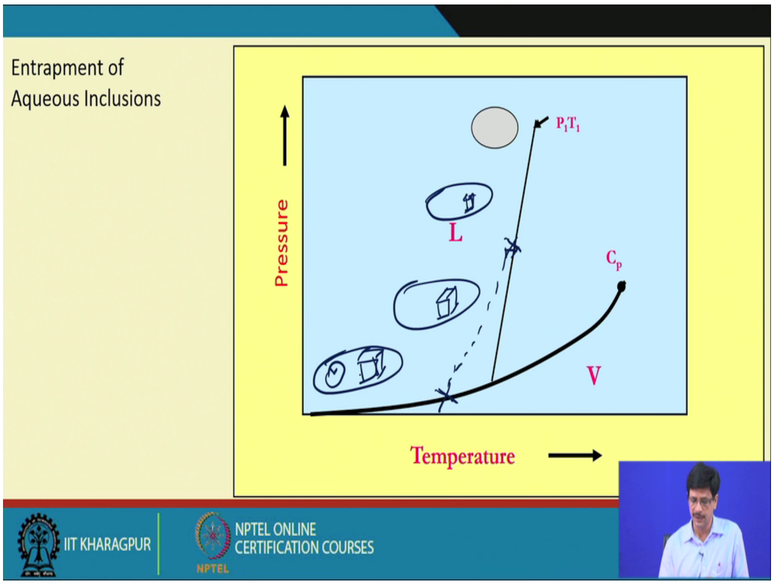

Let us say it has a content of sodium chloride which will make it and with further when the temperature pressure is decreasing, there may be a point there may be a point that is it somewhere here. In which case, in corresponding to that there may be this inclusion in place of just being a liquid, there will be a salt of sodium chloride which will be precipitating from there.

So, that means, the liquid is attaining saturation with respect to a sodium chloride. Now form that point when we further decrease the temperature and pressure condition, it will not follow a constant density curve, but it will follow something like a like a path in which this particular inclusion will have the solid crystal grow a little larger in it size, because they solubility's still will fall with the temperature, and fall in the pressure and temperature. So, finally, when again it will intersect a point on the boiling curve this inclusion will give rise to a vapor and the solid crystal. So, this will be a situation corresponding to occurrence or the polyphase inclusion. Now we will take this up again little bit more details.

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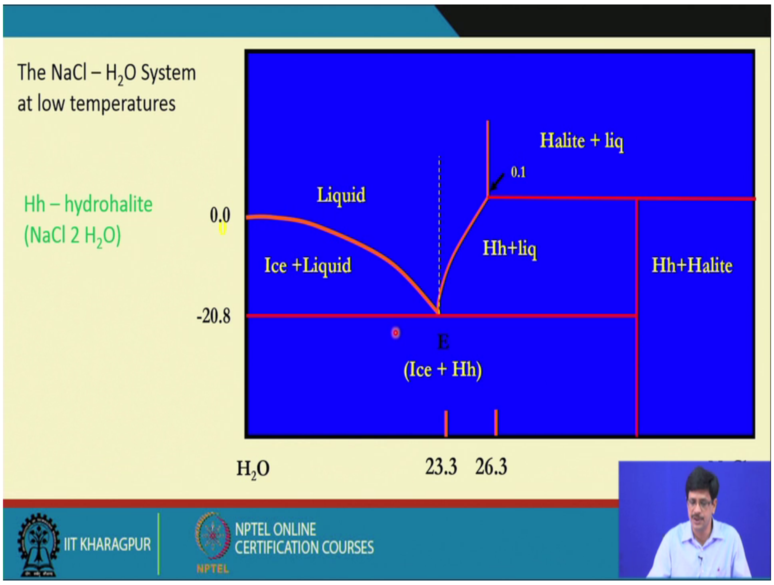

And so, if you now we have only talking about the simple situation of aqueous free without considering the non-electrolyte species. And then we will now the other aspect; that means we are interested in the pressure and temperature condition or entrapment and the other important attribute that you are interested in is the composition.

And as I have said that because of the dominance of the sodium and sodium as the cation and the chloride chloride as the anion and the most extensively studied system is the water salt water NaCl system.

Now, we will see is it possible to say something about the compositional characteristic gross compositional characteristic of the fluid inclusion in terms of the term that we say it is a salinity or in terms of the total dissolved solid, and the dissolved is approximated by sodium chloride. So, this is the binary phase diagram and I hope that most of you are familiar with such kind of binary phase diagram, and this binary phase diagram is H 2 O and NaCl; where are the temperature is now in the lower side this is 0-degree Celsius corresponding to the triple point of water or the temperature at which water solidifies to ice. And this in this downward directions the temperature decreases. This value corresponding to minus 20.8 should be noted here.

Now, what does it indicate is a binary phase diagram which can be interpreted or can be understood in a very conventional way. That if we see this is a liquid field, and as the temperature is decreased with any increase in the concentration of sodium chloride, if the further decrease and temperature will make the composition or make the fluid move on this cotectic line; on this cotectic line the this field is the ice plus liquid.

So, on this will have ice plus liquid as the stable assemblage with further decrease. So now, as we know that this particular liquid will get enriched with respect to the other component that is sodium chloride, because it is moving to the right. And it will go on moving to the right till the point it reaches which is marked as E is the eutectic point. And at eutectic point as any standard phase diagram interpreted it will have the complete a solidification of the liquid here. And the solids that will be forming are the ice plus a hydrate of sodium chloride which is known is the hydro halite which is NaCl plus 2 H 2 O and it is composition.

So, this is the water rich side of the phase diagram. And here the liquid will become totally solidified. Now what will happen if the composition of the liquid is so, this is a eutectic temperature and eutectic mixture proportion is 23.3 weight percent of sodium chloride. And this value which is 26.3 sodium chloride is the room temperature solubility of sodium chloride in water which is marked by this vertical lines. So, here the other fields so, when we go to composition a concentration higher, than the eutectic composition, we are on this arm of the binary.

So, any liquid whose original composition is here, when the temperature decreases and it intersects the cotectic here; this cotectic which essentially be liquid plus hydro halite. This is the field in which sodium chloride 2 H 2 O that is hydro halite that is soluble here. So, this is the hydro halite plus liquid field. And this is the so here as an when the liquid reaches here, a hydro halite will form and on further movement of this line.

The liquid will become depleted or lesser in come lesser in concentration with respect to sodium chloride, and it will again follow the same way it reaches the eutectic point where ice will form along with hydro halite and it fluid will become completely solidified. Beyond 26.3 weight percent we know that it will only be halite stable condition at temperatures, above 0 degree centigrade it will be halite plus liquid.

Here it will be hydro halite plus halite, because any solid halite will be there will get hydrolyzed, and so this is the complete binary phase diagram in on the lower temperature side.

So, then it tells us that by using of this kind of very simplified diagram, it will be possible to approximate the composition of the fluid in terms of the dissolved solid which will be sodium chloride.

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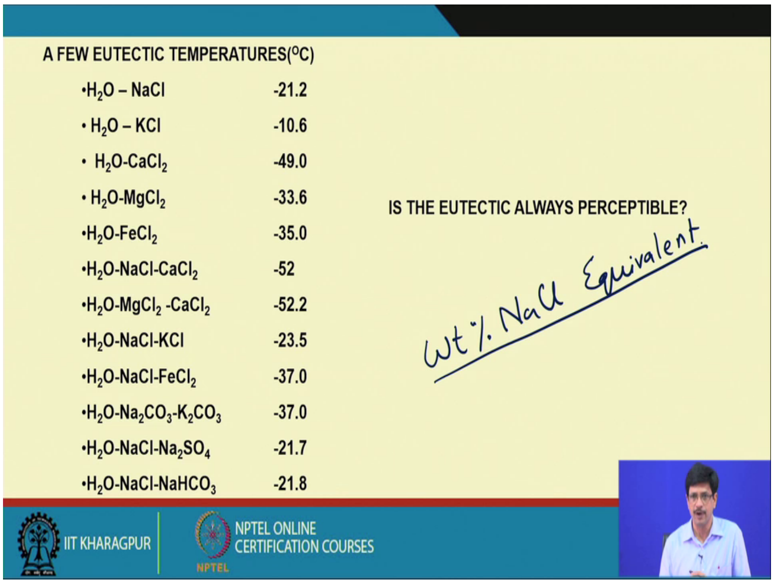

There are standard such depression in freezing point curves, which have been worked out for many other species. The other common species could be potassium chloride, calcium chloride, magnesium chloride, iron chloride; even there are sometimes bicarbonate water, water plus sodium bisodium bicarbonate water plus sodium carbonate, even sometimes it could be sulphate.

So, this kind of this kind of electrolyte species are also possible dissolved species in the in the in the liquid water under crystal conditions of temperature and pressure. So, if you look at such kind of eutectic are known it is not that there not known. The water and potassium chloride eutectic temperature is go minus 10.6. Water and calcium chloride is about minus 49. Water and magnesium chloride is minus 33.6. Fact is that even though this kind of eutectics are known standard are the fact that the crystal fluid as the dominant, dominantly sodium chloride is the electrolytes species dissolved.

So, the freezing behavior of any liquid which is present in the inclusion cavity can be expressed in terms of the sodium chloride weight percent thinking, that the if say for example, sodium chloride is some percentage of sodium chloride plus some other percentage of potassium chloride.

So, the combined reflect of the depression and freezing point will be equivalent to the if the full solid would have been in been, so sodium chloride. And this does not introduce much of an error. And so I have just mentioned a few of the eutectics which are known. But the fact remains that the salinity of the inclusion fluid is always expressed in terms of weight percent NaCl. So, we use a term which is fixed little bit more specific that weight percent NaCl equivalent.

So, whenever we are doing any freezing study of the fluid inclusions, and what we basically can do I can see is that the in a system that we have described in the heating freezing system where we can attain temperature as low as minus 100 and 96 degree Celsius; their getting temperature of the order of between 0 to minus 20 so this kind of eutectic values of course, get revised. So, which was which was been shown here is minus 20.8 possibly has been revised to minus 21.2, but that is immaterial. So, we express them is weight percent equivalent.

So, whenever we record so our observe our whole objective is that we use a micro thermometric apparatus, and we observe the phase changes that is taking place inside the inclusion in response to the change in temperature. And the micro thermometric experiments and we record those as the temperature at which the phase changes have occurred. And whenever we get such kind of so, if we although will be discussing this integrated details.

So, say for example, a temperature corresponding to a points say for example, here so which will be something which will be below 0. So, let us say this is minus 5 so this minus 5 can be translated into a weight percent NaCl. But we know that there could be NaCl there could be other shorts than NaCl and we can express that would be weight percent NaCl equivalent.

So now, as you could see this table there are also ternaries like sodium chloride calcium chloride water; sodium chloride magnesium chloride and water, sodium chloride calcium sorry sodium chloride potassium chloride and water. And these systems are also important.

For example, this water NaCl CaCl 2, because possibly other than next to sodium chloride, the other electrolyte which are common in crystal fluid are a calcium chloride and potassium chloride. To some extent also magnesium chloride and iron chloride also could be an important species.

So, what generally so will see that these ternaries are also their eutectic temperatures also known. We will discuss what exactly they are the ternary eutectic means a same thing, whenever we have a liquid where bring it to a completely frozen condition that corresponds to ideally to be the eutectic temperature. And that kind of eutectic temperature will be definitely different from the eutectic temperatures in case of the binary like sodium chloride. And whatever value and there are ways to know to reach at the eutectic temperature through the micro thermometric experiments which will be elaborating later.

So, the only indication that it can give us about the chemistry of the inclusion fluid is that, if the temperature at which the inclusion is coming to at complete frozen stage is way below, temperatures corresponding to any of the binary eutectic, then we only can say that this particular inclusion liquid contents electrolyte species other than sodium chloride, ok. So, we will continue discussing on the on further on this micro thermometric principles in the coming classes.

Thank you.