# Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application Prof. M K Panigri Department of Geology and Geophysics Indian Institute of Technology, Kharagpur

# Lecture - 15 Aqueous Fluid Inclusions (Contd.)

Welcome to today's lecture. So, during the past 4 lectures, we were discussing about the response of aqueous inclusions to heating freezing in a micro thermometric apparatus and we know that we have studied them in chips made out of the vapor of the sample that we have considered, which have been sampled from, which have been taken from a entity, like any particular rock unit in the crust or an ore body and some such locations where we want to study the geology, we especially in particular reference to the characteristic of the fluid and the way the fluid evolved.

And also to ascertain the probable origin of the fluid, which give rise to the ore or the rock as our interest maybe. We have seen the aqueous inclusions the aqueous biphase liquid plus vapor inclusions and the aqueous polyphase inclusions containing daughter crystals of sodium chloride that is halite sometimes with more than one daughter crystal like sodium chloride and potassium chloride, which is sylvite and in some such situations, we can understand the response to heating and freezing with help of non phase relationship in such kind of fluid mixtures.

So, fluid inclusion studies in a way has makes us go through or to have a good understanding on the, on such phase relations which are very essential and it is also that the fluid inclusion is in order to interpret and make the best use of his micro thermometric data, we will always be taking help of such kind of phase diagrams, phase relationships. And as we know that the fluid in the earth crust giving rise to the rocks or the mineralization ores are very complex fluids containing multiple anionic and cationic species and craft at variable pressure temperature conditions.

And after the entrapment process, they undergo post entrapment phase change and we see them in various combinations of liquid plus vapor or liquid only or vapor only or liquid plus vapor plus one solid crystal or more than one solid crystal. Till so, far we have been able to make out understanding clear as to how to use the microthermometric data for volumemetric measurement of the inclusion fluid in consideration. We freeze them and then note down the melting temperature of ice or hydrohalite.

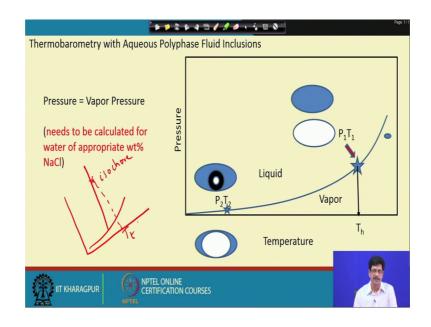
And in case of a polyphase inclusion like halite or sylvite bearing inclusions, we note down the temperature of dissolution of the solid crystal and then calculate the chemistry biochemistry in terms of the weight percent NaCl equivalent of a particular aqueous inclusion and with the value of the weight percent NaCl equivalent and the temperature as it may be in case of a biphase inclusion it is the liquid vapor homogenization temperature or in case of a polyphase inclusion, it is the dissolution of the daughter crystal if it is higher than the temperature of homogenization.

We use this and you standard formulation that have been, formulated based on limited volumetric measurements made on such kind of fluid mixture and such kind of experimental data are available in the literature and.

So, with some empirical fitting of the experimental data the PVTx relationships can be formulated and there can be used to calculate the density and once we know the density of the aqueous inclusion, we also use formulations which have been worked out by many workers in this, in fluid inclusion research to calculate the isochore, the slope of the isochore the dP dP by dT slope of the isochore. So, that we can construct the isochore of such inclusions in a p t space and that is exactly is the exercise that what we call is a thermobarometry.

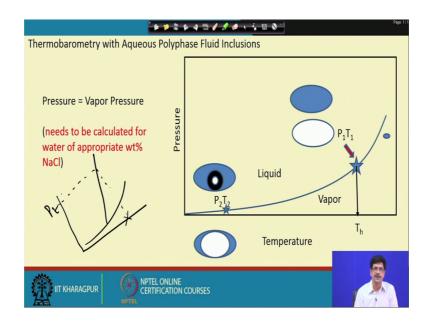
So, when we record the measurements in our experiments there the microthermometric data and what we essentially you were looking for is to ascertain the temperature and pressure conditions of the fluid intern the conditions the pressure temperature conditions in which the minerals are formed in the earth crust.

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So, we have discussed the situations pertaining to the liquid rich inclusions and also we know that there are, there could be inclusion, which could be a tapped as vapor from the vapor stable field and they are manifested as liquid plus vapor with a very large or a very high proportion of the vapor and they are the vapor rich inclusions, which homogenized into the vapor phase. In case of the aqueous liquid inclusions, we also in case of the aqueous liquid inclusions where we, we discussed that once we have an isochore if we have any independent estimate of pressure, we can get the temperature for the formation which you know as the temperature of trapping.

And which sometimes can be done in situations, where there are some independent barometry same is also could be true if there is some independent geo thermometer, in which we can also do this reverse process that if we knowing the temperature, you can also like. (Refer Slide Time: 06:59).



If this is isochore, then if we know that the temperature of formation of a particular mineral is a somewhere here there we can also knowing know the pressure by so, this will be the pressure of tapping. So, this is essentially the exercise which is the, which we call as thermobaromety in fluid inclusion.

Now, on this diagram, we will try to see that whether such kind of thermobarometry, exercise can be can be done in such a way that we would not be needing any pressure correction, the previously we discuss that if on the isochore if we have a pressure known at any point we drop a perpendicular to the temperature axis and get the temperature of trapping and difference between the temperature of trapping and the temperature of homogenization is something which gives us an idea about how much of correction would be made, would be required to our temperature of homogenization to know the true temperature of trapping.

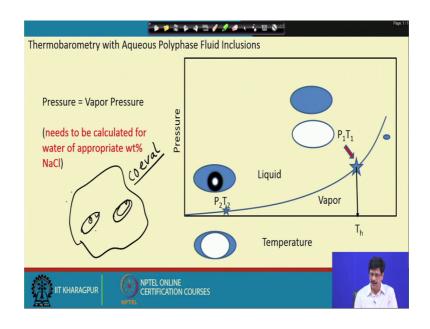
Now, there could be some situation where we will not be needing any pressure correction and that is situation, which is depicted in the on this diagram. So, it will be a thermobarometric exercise with aqueous inclusions there will be actually on aqueous biphase inclusion. So, here the pressure will be equal to the vapor pressure, now what the condition could necessarily be, as we know that the condition is necessarily that this is the boiling curve, where that is coexistence of liquid and vapor, this is a critical point here some of this dot is below that. So, here we imagine a situation where the fluid in the subsurface any anywhere in the earth crust where the fluid is being generalized. Because of some physical process where there is sudden movement of the fluid a packet of fluid well lower to a much shallower condition the temperature is high then the fluid will essentially go a process, it will be there will be a coexistence of liquid and vapor and we will call this condition is a boiling situation which will discuss a little later about the significance.

But this essentially indicates that the mineral growth process the entrapment of the fluid inclusion was taking from a fluid, which was in its heterogeneous condition, but again we you stick to our assumption that the entrapment is homogeneous, means on these particular point when there is a host crystal which is crystallizing, which precipitating will entrap either the liquid either packet of liquid or a packet of vapor not a mixture of the two.

So, in that case as we discussed before if a vapor is entrapped inside it in the solid crystal lattice then we decreasing temperature in pressure condition, it will give rise to inclusion which will have a large proportion of the vapor is shown in the inclusion, which is below here and the liquid, which will be trapped here we will also be evolving on the liquid vapor curve and then finally, it will be at room temperature we see them as a liquid rich inclusion with a smaller proportion of the vapor.

In the situation is that when we heat these two inclusion and then the necessary the ore the, the necessary condition for such kind of a situation is that if this is the host crystal.

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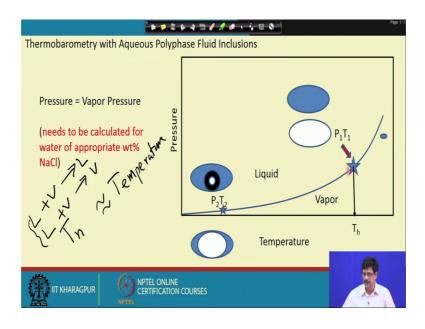


Then these two inclusions wall which will be a very vapor rich inclusion like this or one which will be a liquid rich inclusion like this, these two inclusion like shown here by these two sketches, they have to be coeval. Coeval means there should be should have been trap at the same time at the same conditions within this within the single crystal of the host mineral, this is, this represents one single grain of the host crystal within the single grain need not necessarily we have to when the same plane, but have to be a part of three dimensional network random three dimensional network not trail bound. In this case these two inclusions which are coeval, one is a liquid rich inclusion with a small vapor bubble and the other one is a vapor rich inclusion with a very negligible proportion of liquid.

If there heated then both have into homogenized, in this case when both will homogenize, this homogenization the first inclusion here, the one which is shown as the one liquid rich inclusion with a small vapor bubble will homogenized as before as you have discussed the homogenization behavior of a liquid plus vapor inclusion which homogenizes L plus V to L. So, this is will homogenize into a liquid phase.

The inclusion which is shown here will also evolve with heating along the boiling curve where the liquid phase will go on diminishing and its amount and the homogenization at the homogenization state it will be the cavity will be completely field by vapor. We will also discuss about the practical practicality of noting down the temperature of homogenization where it the homogenization is L plus V to V where there may be a little bit of uncertainty.

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So, here the condition is that the homogenization temperature that is these; this L plus V to L and L plus V to V both these homogenization temperature which is the T h have to be same. So; that means, this the liquid at the homogenization, which is giving rise L plus V to L and the L plus V to V have to be the early at the same temperature.

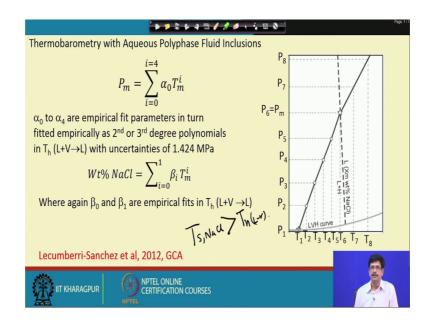
So, the necessary condition is that these 2 inclusions have to be coeval primary, they may be also made in cases where there secondary where belonging to the same generation can also be utilized. There to be coeval and the temperature of homogenization of these 2 inclusions, one to the liquid state, in the other to vapor state have to be, have to has to take place at the same temperature at least within the acceptable uncertain limit of plus minus 1 degrees Celsius.

So, that is, that is a situation in which then we would not be requiring any pressure correction so; that means, here the then homogenization temperature of these 2 inclusions, which takes place at the same temperature does not need any pressure correction and the pressure on this boiling curve will be the vapor pressure of the water of a of the specific, of the specified weight percent NaCl equivalent because we would have measure the salinity of the liquid in this case in this case both by, by the depression of the freezing point of the ice, depression of the freezing point that we discussed before

and the salinity is known and then that particular salinity the vapor pressure of the of water can be calculated. As we know the maximum vapor pressure can go in case of a liquid vapor pressure coexistence to 220 bars that is the critical point and anything below that.

So, if suppose this particular the point corresponds to 100 bars pressure and if we establish that this particular pressure is hydrostatic pressure, then we can calculate that what are depth; what is the depth at which this process took place of where the mineral formed?

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there is there the in case of the aqueous polyphase inclusion with halite daughter crystal it is also possible to do thermobarometry, but here the only situation is that if you look at this diagram on this diagram as we discuss before this if a situation in which this is always will be corresponding to situation where d T s NaCl that is the temperature of dissolution of the halite should be greater than the temperature of liquid vapor homogenization as we discuss before that ye, its already, its mentioned here that the T h the this in this case the temperature of homogenize temperature of dissolution of the daughter crystal T s NaCl should be greater than the T h L V, they could vapor homogenization and under that situation are the this particular method of estimating pressure from the halite dissolution is applicable.

So, here on the diagram what we see that an inclusion, which initially had liquid plus vapor plus 1 ne daughter crystal of halite that is sodium chloride it underwent liquid vapor homogenization and the homogenization to liquid at a point corresponding to let us a T 1 and that is equal to the T h and after the disappearance of the vapor phase, the system evolves in a liquid plus halite field.

So, during the evolution of the liquid plus halite field the halite crystal keeps on dissolving in more and more amount and it volume reduces and it reaches a point where the liquid the halite completely dissolves where it is written as P 6 and that is as the P m is corresponding to the pressure at the melting of the halite or dissolution of the halite and it moves through in this liquid vapor curve and reaches to the point here.

So, as before we could also approximate the entrapment condition entrapment pressure and temperature condition from the dissolution temperature of halite as a minimum approximation because from here onwards the inclusion again will follow a constant density isochore as shown here. For example, temperature corresponding to T 7 and T 8 and we will not have much of a constraint here to exactly know at what point the inclusion actually form in absence of any other independent consideration like a barometer or a thermometer, which we discuss before.

But then this particular situation it was initially crude method was devised in which the sodium chlorides properties of thermal expand the coefficient of thermal expansion the amount of sodium chloride the dissolved from T 1 to T m T 6 let us on T 6 the T 6 corresponds to temperature at which halite dissolve. So, corresponding to T 6 the and then change in the volume of the host crystal and then the total amount of weight percent NaCl equivalent that could be calculated on the basis of the dissolution of this halite crystal.

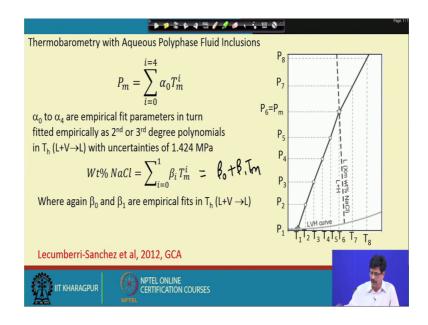
Some crude method were devised from which some standard tables of volumetric measurements experimental data if the a value of the vapor pressure because this pressure also will be the vapor pressure at the dissolution of halite corresponding to temperature of T 6. There has been some recent work as a referenced here, the there has been formulation on the pressure at the dissolution of halite melting of halite is P m.

Is given as this expression in which this alpha coefficient alpha 0 to alpha 4 have been or empirical fit parameters and these are these have been fitted as second or third degree polynomials in T h, where the is necessary condition is that the temperature of homogenization has to be L plus V to L because this corresponds to the situation where it will be liquid plus halite stability field, it is not worked out on the vapor plus halite stability field and such kind of formulation also has an uncertainty of a would 1.42 for mega Pascal means the transits about 14 bars of pressure.

And these authors also have given a revised method like the one we discuss before that the salinity of an aqueous inclusion with homogenizing by a method by disappearance of halite, where the salinity could be calculated from the temperature of disappearance of halite or melting of the halite is a second degree polynomial in temperature with the, with a equation almost like a 0 plus a 1 T d or T s plus a to T s square so on.

So, this one this equation was also devised as an improvement where weight percent NaCl could be represented as a beta 0 plus T m plus beta 1 beta, beta 0 because I is equal to 0 here beta 0. So, this equation will be something like of the type of.

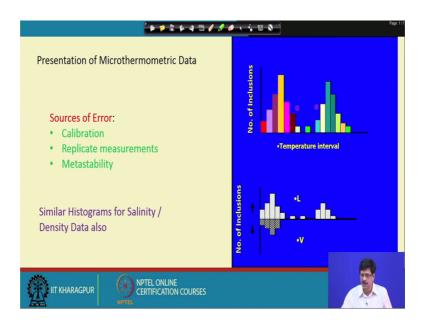
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So, weight is equal to something like beta 0 plus beta 1 T m and this beta 0 and beta 1 these coefficients are also fitted as empirical fields to temperature of homogenization.

So, that the; that means, us to a we conclude that what are the possible thermo micro thermometry parameter microthermometri C data that could be acquired on the aqueous inclusions in case of if I if we will rerivit, but before that.

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So, the coming to the concluding part of it, that what how, how what how could use, it how could we represent the data microthermometric data. So, this standard practice of presenting the microthermometric data is by the method of histogram and on a histogram we know that we choose something like a class interval and then calculate the frequency in terms of here as shown here the number of inclusions and suppose this kind of histogram is prepared for both for all the data, that we generates salinity temperature of homogenization and also the density to be calculate for the inclusions.

So, we keep in our mind that when we coming to stage where to present our data means we have acquired the data, there we intended to do in a particular considering the problem that we picked up the samples, the number of samples that we decided to work on and for sample the number of inclusions that also we wanted to work on we have finish the data acquisition and now we present them.

So, this presenting the data only with an intention to look at the kind of pattern of distribution that we see in the data for example, it is shown here that, if we and since it is statistics. So, we have to go by the basic rule of as to how the class interval has to be chosen, this class interval for the guiding factor for the class interval is essentially the minimum value and the maximum value. Let us say for example, we in the course of our acquisition of data we find that the salinity is starting from very close to values of 0 let us seven point 1.2 or 0.5.

And can go up to 40 50 60 even 70 weight percent NaCl in any specific cases and then we are we think of choosing a class interval and then calculate or the values the number of inclusions following in the that particular class interval and we plot a histogram, see histogram is plotted with only the intention to see whether we get a single unimodel distribution of the salinity or we get as you shown here, that is for example, if we see here then this kind of a distribution we call as a bimodal, means the there, is there are two distinctly different salinity values will moderately low or low or to low to moderate kind of a salinity value, suppose for example, if a; if I divide this range into 4 weight percent interval, then it will be 0 to 4 8 12 16 20 24 28 32 36 40 and so on.

So, we see that they there could be a bind this kind of distribution is basically interpreter bimodal distribution, it gives have some idea that well then there must have been some because essentially we also have to keep it in our mind that, when we see the inclusions and we are essentially trying to understand the primary phenomena of the formation of the particular over a rock then essentially when you are looking at fluid inclusions and then we know that there a result or a manifestation of the position means the spectrum the fluid characteristics during which that particular mineral form mineral crystallize the fluid changed in this characteristic in this way.

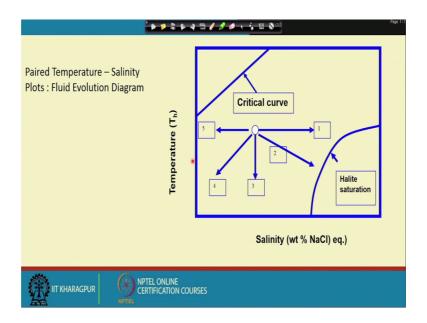
So, that could later on be this there could be a assigned as to what is change could be interpreted is whether there 2 different types of fluid or the same fluid possibly would I evolve in such a way that at one particular condition it was very highly brine, highly concentrated brine and then the evolve down to and again at an another value and or to or to be more specific depositional process was more.

I mean extensive in corresponding to salinity values it is shown here with continuous deposition of the particular mineral, which are in which has been and if we take it for granted that there has been no bias in our sampling of the fluid inclusion and we have chosen the right fluid inclusion that also itself is a practicality of fluid inclusion study to choose the right inclusion not to have been leaked earlier and away from heal cracks for the primary inclusions for the chances of the content of the inclusion being later destroyed by later activities such kind of situations or minimize and we are able to plotted them a histogram.

So, whether it is a temperature or salinity or density we can plot them is histograms as shown here. So, here on the diagram below we see that this histograms are plotted in such a way that there on the either side of the axis of this if an we dividing them. So, with two different types of legends one sometimes when we have in the aqueous biphase inclusions inclusion, which have both liquid rich and vapor rich and also we get situations where the vapor is inclusion homogenize into vapor state then their data can be interpreter you are presented in this way.

So, that it gives us an idea there well there are into aqueous inclusion which homogenized into both modes and if in an idea very ideal condition where you could see that the frequency of the mode for occurrence of a liquid phase homogenization is also coinciding with vapor phase homogenization and we also keep it in mind that, we do the we have taken the coeval liquid vapor inclusion then we go on to interpret important physical process say for example, boiling in this case.

So, we will see such some of the case studies where in any of the different types of situations, where such kind of histograms are routine procedure for presentation of microthermometric data to understand the fluid characteristics.



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And then again we have a paired data on temperature of homogenization and salinity in some situations people also do plot is the T m; that means, the depression in freezing point on the success also, but it is always a good practice to its a choice I mean generally

we prefer to draw this diagram on temperature of homogenization of salinity. Before interpreting this diagram you also know that these temperatures are the temperature of homogenization, which are not corrected for pressure because we did not have any other independent parameter available with us.

So, these diagrams are very popularly known as a fluid evolution diagram on this temperature and salinity diagram because here we understand that the what little bit of deficiency what we have because of non availability of pressure correction, will be somehow compensated by the statistics of measuring hundreds of such inclusion in a particular sample, particular environment which in which we are more interested to have a look on the what is the range in values of the temperature and salinity in which the deposition process occur.

So, on this diagram this top part is a critical curve, which we know that this corresponds is about 374 degree celsius for a pure water and we, we can calculate the critical temperature at varying concentrations of NaCl and this critical curve is plotted here and this one is the halite saturation curve means this corresponds to 26.3 weight percent at room temperature and as the temperature goes on increasing on the success in the with the solubility of NaCl goes on increasing and that is not this curve is labeled as the halite saturation curve. Ideally when we talk of by aqueous biphase inclusions their likely to be falling in these regions aqueous polyphase inclusions with halite daughter crystal are likely to fall on this halite saturation curve.

But at times we also do get fall aqueous biphase inclusions to points fall beyond the halite saturation curve without actually having halite daughter crystal in them and which happens, because the there is the chemistry as been such that the halite daughter crystal could not precipitate is independently is halite daughter crystal, but because of presence of other soluble salts other chlorides the. So, the solution is actually very brainy it would be a sylevite percent NaCl equivalent could be more than what could be corresponding to the saturation value.

So, now more important here is the what we say is the evolution, the fluid evolution path that that we think of the fluid, fluids in the earth crust and evolving to in some specific way that either the fluid could cool or the fluid could boil or the fluid could mix. So,

fluid mixing is a very very common phenomena in crustal processes and there are many ways the fluid mixing is manifested.

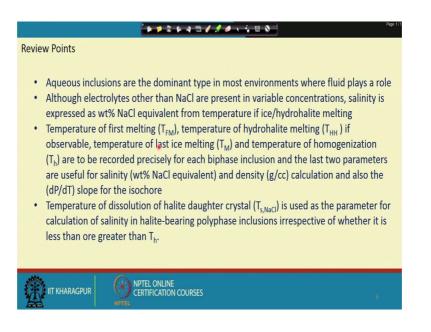
So, this is this is an ideal as diagram considering the white circle which is to be the original aqueous fluid what will happen if the fluid and suppose this particular fluid has got a temperature and salinity value and this salinity value will have kind of an inverse trend decreasing value for both temperature and pressure, temperature and salinity and if we with these kind of temperature also helps us in understanding the fluid ancestry for example, a particular fluid is having a very low salinity and low temperature it is likely to the meteoric water, which is where the it is almost the phase sleep precipitated water rain water which is just percolated through the fractures in the fracture network in the rock and is just not that is low in it salinity and also not that very high in the temperature.

And as the guess that that fluid could be very high temperature and salinity which will be discussing later on and this kind of a trend would tell that possibly there was some fluid mixing process. Even we can have the line, which have shown by arrows towards 5 or to 1 this also could be trends possible in fluid mixing of low saline and high saline fluid which also happens, it could be fluid which is very high temperature, but low saline is it happens in a metamorphic fluid.

Now the most interesting part or most interesting path of evolution of a hydrothermal fluid is by boiling means from at originally homogeneous liquid vapor phase get separated as when the temperature decreases, sorry pressure decreases with temperature with very little fall in temperature in adiabatic condition in that kind of situation, the vapor phase get separated out of the liquid.

So, has not with the vapor phase get separated out of the liquid because of the very low concentration of the salts in the vapor phase, the residual look it becomes more and more rich with NaCl. So, that gives a trend of increasing salinity with very negligible change of very little change in the temperature of the fluid we get a very high salinity trend and that is say boiling case, but as we before we said that boiling coming for with accompanying evidence of coexistence of coeval pure aqueous biphase inclusion fluid liquid rich and vapor rich and that those two inclusions would be homogenizing at the same temperature.

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So, here some of the review points that aqueous inclusion of the dominant type in most environment where fluid phase a role all though electrolytes other than NaCl at present in variable concentration salinities always expressed NaCl weights percent equivalent.

That is not a serious deficiency, but in definitely introduce a some amount of error in calculating in annoying the exact salinity value and the temperature of host melting that gives us an idea as to whether salts whether that is pure sodium chloride or salt other than cations other than sodium are present and the temperature melting of ice is used to calculate the weight percent NaCl equivalent that the salinity of the fluid total dissolved solid and the temperature of dissolution of solid crystal that is T s NaCl is used to calculate the salinity and also the density is calculated from temperature and salinity.

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Review	Points
· · ·	It is possible to have both temperature and pressure values from homogenization of aqueous biphase inclusions if trapping was from a fluid that was boiling at the time of deposition of the host mineral A minimum pressure of trapping can also be determined from halite dissolution temperature $(T_{s,NaCl} > T_h)$ Isochores are useful and help in determining trapping temperature if pressure of formation of the host mineral is known OR trapping pressure if temperature of formation of the host mineral is known. Pressure correction for homogenization temperature is more significant in case of low- salinity (low density) inclusions whose isochores are less steep Paired salinity- $T_h$ plots not only give important clue on origin of the fluid, but also, indicate the way the fluid evolved. It is extremely important and beneficial to understand the phase relationship in the H <sub>2</sub> O-salt systems for better appreciation of fluid inclusion thermobarometry.
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So, it is possible to have both temperature and pressure values from homogenization of aqueous biphase inclusion is trapping was from a fluid it was boiling, it is possible to do barometery with the halite bearing daughter crystals, halite bearing fluid halite daughter crystal bearing fluid inclusions where the T s NaCl necessarily has to be above T h because if T s NaCl happens to be below T h then what we are getting at the homogenization is actually is a liquid it is on the boiling curve and we know that it will follow isochore where the temperature and pressure cannot be further constraint.

So, isochors are useful and help in determining trapping temperature the pressure of formation of the host mineral is known or trapping pressure if temperature is known we have discussed pressure correction of homogenization temperature is more significant in case of fluid which is a very low salinity, but there generally pressure corrections are low in case of high salinity and high density and the paired salinity T h salinity T h plots are not only give the important clues in the origin of the fluid, but also indicate the way the fluid evolve like a fluid mixing fluid boiling or even simple cooling sometimes also is an efficient process in bringing about the position of many minerals.

And the study of fluid inclusion actually leads us to understand the intricacies of the phase relationship in the complex brines water with variable amounts of different types of electrolytes. So, that brings us to the end of the discussion on the aqueous inclusions and we will see them later again in different while discussing some different case studies.

So, that, we will continue discussing on the other types of inclusions in the subsequent classes.

Thank you.