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

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Lecture - 39
Review of the Course

Welcome to today's lecture. We will continue our discussion on the aspects of the computer programs or software for fluid inclusion data. We just saw the formulations for the aqueous fluid, for calculation of it is of the density and the iscochore and doing any kind of thermo gravimetric exercise, the computer programs could be accordingly written. So, just to continue the discussion what for the other type of inclusions let us say it is a carbonic or an aqueous carbonic inclusion.

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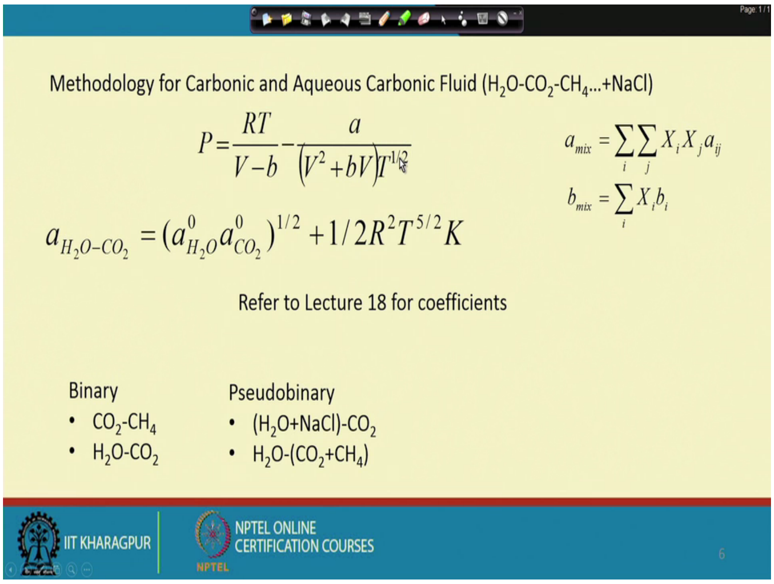

Methodology for Carbonic and Aqueous Carbonic Fluid (H_2O-CO_2-CH_4...+NaCl)

$$P = \frac{RT}{V-b} - \frac{a}{(V^2+bV)T^{1/2}}$$

$$a_{mix} = \sum_i \sum_j X_i X_j a_{ij}$$

$$b_{mix} = \sum_i X_i b_i$$

$$a_{H_2O-CO_2} = (a^0_{H_2O} a^0_{CO_2})^{1/2} + 1/2R^2T^{5/2}K$$

Refer to Lecture 18 for coefficients

Binary
- CO_2-CH_4
- H_2O-CO_2

Pseudobinary
- (H_2O+NaCl)-CO_2
- H_2O-(CO_2+CH_4)

There we there also we do have a, we have quite a number of formulations which have been developed over a period of time. Like the one which we discuss before is like a readily it is call an equation to account for the non ideality, non ideal parameters like this a and the b parameter which are the non ideal parameter from deviation from the ideal gas equation and that is kind of equation like readily it is call an equation.

When it is converted into a semi empirical kind of formulation taking to account the theoretical basis such as the interaction of these molecules as hard spheres and taking to consideration there forces of attraction and the potentials. And, the observed the values on the volumetric properties. One of the problem is that the experimental data on carbon dioxide bearing fluid are much less compared to what are available for to your aqueous fluid.

If you have any aqueous carbonic inclusion or a carbonic inclusion we still we can use this particular equation for calculation of the density and the pressure. And, also the once we know the equation are the if I calculate the parameter which is a and b and also solved for the molar volume then we can always calculate the slope as a d p by d t.

And as one can see that this d p by d t slope will not be very linear and that is what we experience where we calculate for a pure carbon dioxide, this a and b parameter will be representing the pure species. For example, the a for CO 2 which is a function of temperature, which was shown before and also for mixtures which are worked out to be a product of this term are depending on the species that represent.

If there are 2 species then it is a double summation term with the non ideal term a as coming out to be the individual terms plus aqueous term which is a H 2 CO 2 incase of H 2 O, CO 2 fluid on if it is an H 2 and NaCl CO 2. Then we consider them to be pseudo binary and take the aqueous component as H 2, NaCl with fixed to weight percent NaCl and the carbon dioxide is the other component and also calculate the mixing parameters a and b.

And so, these were elaborated in the previous lecture 18 or the coefficients what we did not show where the weight percent NaCl dependent expansions for the a and b parameters for water which one can always look up from the who is doing for a water NaCl CO 2 system. And, such kind of parameters need to be worked out for the binary if it is a CO 2 to CH 4 or H 2 O, CO 2 and pseudo binary like H 2 NaCl CO 2 and H 2 O and CO 2 CH 4 and these parameters are worked out so, the then the density which can be calculated.

So, given the composition if we know the mole fraction of the components like carbon dioxide and water in any fluid mixture then this a and b parameter are worked out at any particular temperature. And then these equation which can be expanded as a cubic equation and V can be rewritten as a equation cubic equation. And V can be solved my standard numerical technique and the molar volume could be calculated from the molar volume one can calculate the density.

Because there inverse molar volume is the specific volume the specific volume and then the molecular weight will give you the grams per c c volume in terms of grams per c c sorry the density in grams for c c. And the isochore the slope would be calculated for this particular fluid or a fluid mixture and pressure at any temperature could be calculated from the isochore by doing extrapolation has been shown.

So, that is the these are the implementation which has been done in the softwares which were discussed and as it is espresso where there are many variations like for example, a virial equation or there are many forms many different forms of this equation for state to account for the non ideality in the mixing of this fluid mixture have been proposed there they can be used. But the one which has been implemented what has been shown from the example of the software that was demonstrated is the one which is used here.

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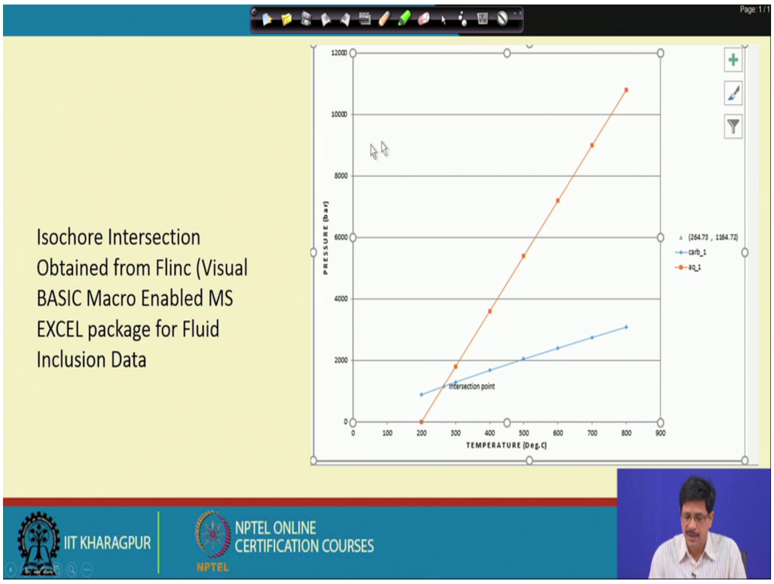

Isochore Intersection Obtained from Flinc (Visual BASIC Macro Enabled MS EXCEL package for Fluid Inclusion Data

So, the by using the Microsoft Excel Visual BASIC macro based software package that I just mentioned, but could not demonstrate because of the version mismatch problem here. One could see here that this is the iscochore intersection obtained from a software program which you provisionally named as Flinc. It still under in the process of development and this Visual Basic Macro based Microsoft Excel package for fluid inclusion data.

This represents one aqueous inclusion whose isochore is drawn by using the formulation as discussed, this is the isochore for the carbonic inclusion co existing carbonic inclusion. And the provision has been made to check whether these two could intersect and if the intersection is possible then what is the intersection value as has been shown here.

For example, this is aqueous inclusion isochore is the carbonic inclusion isochore and they intersect at a temperature your 264 and a pressure 1164. This is how we derived or we reduce the pressure temperature path of evolution in a fluid whether it is in an mineralizing system or in any other crystal environment like metamorphism or deformation. If we get several such intersections corresponding to coeval inclusion pairs then we can have these values. So, once these are the Microsoft Excel generated graphs they could all do the customized depending on the user's requirement.

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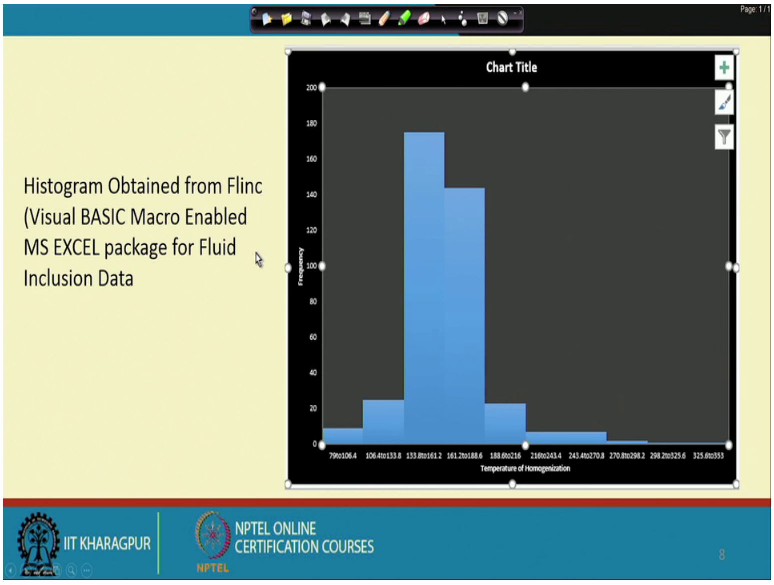

Histogram Obtained from Flinc (Visual BASIC Macro Enabled MS EXCEL package for Fluid Inclusion Data

This is of example how a histogram is generated the demo could not be shown because of the version mismatch here. But this kind of histogram also a generated from the program or this of the graphical user interface base packages, which is developed or can be developed by anybody who has an interest in writing programming, writing programs on the codes and can explore the different functionalities of different environment that is available like, whether it is a visual basic or visual C plus plus.

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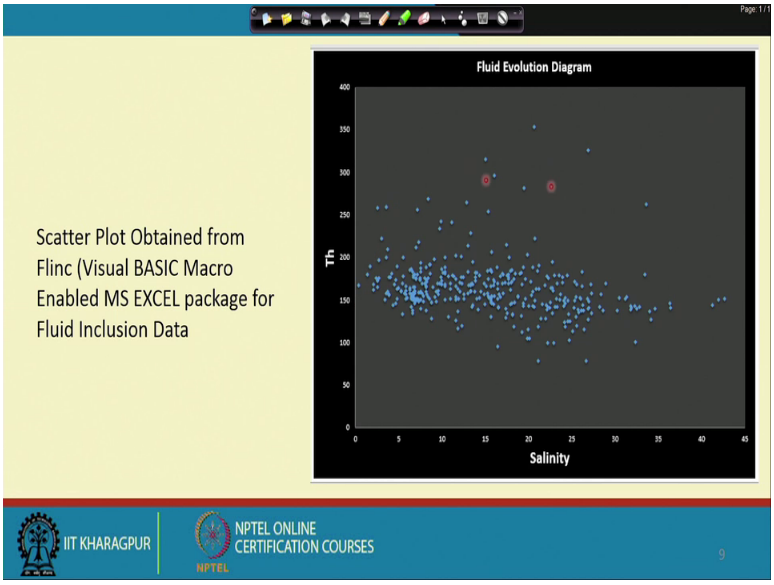

Scatter Plot Obtained from Flinc (Visual BASIC Macro Enabled MS EXCEL package for Fluid Inclusion Data

And also a fluid evaluation diagram which is also can be generated by the table of data which was shown. On the temperature of melting of the depression in the freezing point and the temperature of homogenization and using the equation of state for H 2 NaCl fluid and then taking up taking the 2 fields for plotting of this kind of data which is essentially inherent feature of Microsoft Excel which has been used.

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Review

- Fluid Inclusions are extremely useful geological samples that are a store-house of hidden information on origin and evolution of rocks in diverse geologic settings
- In addition to their tremendous academic importance, they are also of high utility value as aid in mineral and oil exploration
- A good understanding of phase relations in complex fluid mixture (P-V-T-X relationship) is an essential pre-requisite for Fluid Inclusion research
- A sound knowledge and inclination towards instrumental methods is an added advantage for a fluid inclusionist – managing a heating-freezing system itself needs a lot of involvement

So, that brings us to the close of the lecture series on the on fluid inclusions, in minerals, the principles method, practice and the application where we have discussed the basic. I mean for any beginner who is intending to adopt this particular technique for solving the problem that one is addressing, it is a problem of mineralizing system, the work fluid and (Refer Time: 09:39) the fluid of evolution or mineralizing system or metamorphism or a deformation.

So, now, it is time that let us take a review of the discussions that the issue that we have discussed. And the just to just to have some points to recapitulate that the fluid inclusions are definitely are there very extremely useful geological samples that are their storehouse of hidden information on the origin and evolution of rocks in diverse geological settings. And as we have said before that this is only means by which the fluid is actually being directly sampled and we believe that it is independent of the actual timing of formation of the rock.

If the rock is preserved in the earth crust for several hundreds or thousands millions of years of time and that we are sampling them on the surface want their exposed way often, then we are we feel that they are still the remnant of the ancient crustal fluid. And there are many situations like say for example, the work done on there are on the issue of complex in green land by analyzing fluid inclusions in the in quartz of the one of the you rock you needs for (Refer Time: 11:08) complex. There were proposition about the nature of the ancient sea water or what was the net, what was the characteristic of the Achaean sea water. And such kind of conclusion such kind of a interpretations could only be made because we are able to directly sample the ancient geological fluid.

As you have said that in there of tremendous academic importance, because we are trying to address basic issues of basic geological problems and that is how their tremendous academic importance, but it is not only confined to just that they are also a of high utility value as aid in mineral and oil exploration. We have not been able to elaborately discussed or take up the topic of petroleum exploration using fluid inclusion, because petroleum exploration it always needs that the experts who are the experts on hydrocarbon to also be consulted.

But then from fluid inclusions it is only we can only look at the their utility. We can only see them exactly the way we see them see the fluid inclusions in any ordinary rock or a water quartz grain or different types of host minerals that we have discussed. The only difference in the fluid inclusions which are there in the sedimentary basins the petroliferous basins is that they are present as the digenetic fluid, sometimes in the authigenic over growth of the plastic sediments like a sandstone is which the reserve a rock and in that the oil or the hydrocarbons are also present within the fluid inclusions.

So, these hydrocarbons when they will be observed under ordinary of a microscope with the light in the visible range they may not be very distinct or rubious. So, that is why they need to be studied they do have a very characteristic fluorescence when they are studied in ultraviolet light. So, they need specialized microscope for their observation any petrol logical microscope which is equipped with the attachment for studying fluorescence with u v light there will be the ideal one for studying the or looking at the fluid inclusions.

And from the fluorescence characteristics the typical the hydro carbon species which could be the light or the heavier hydrocarbons or sometimes the vitamin which is present in the form of black inclusions which I showed a from some of the fluid inclusion from Mississippi valley deposit. So, these fluid inclusions could be studied and once their composition is determined by the similarly by looking at them and see the fluorescence characteristics and then characterizing them through micro analytical non destructive techniques by Raman spectroscopy. And also obtaining the homogenization behavior, from that the I looking at these inclusions in to fracture spaces which were generated in different time then the maturity of the hydrocarbon and the migration path could be determined and their of utility in oil expression.

So, exact and there are many different literature I mean there available in the public domain where the many such situations could be seen you all the fluid inclusions in authigenic minerals in petroliferous sedimentary basins. So, through the topics that we have covered one thing is very clear that fluid inclusion research or fluid inclusion study does need a good understanding one has to have a good understanding on the phase relations in complex fluid mixtures the P-V-T-X relationships which is an essential pre requisite for working on fluid inclusions.

And as we have seen that till today the there are many areas many gaps and many limitations which are still visible in the formulation of the appropriate P-V-T-X relationships in complex fluid mixtures and to formulate accurate equations of state in pure aqueous system or aqueous plus carbonic systems.

And only we will be applying so, it becomes a challenge for the people who are doing the fluid inclusion work to understand the intricacies and also to attempt to develop verifying the P-V-T-X relationships in different fluid systems. So, and it as it is also quite clear let us have knowledge and inclination towards instrumental methods is an added advantage of a fluid inclusionist.

Even we know that a managing a heating freezing stage itself is needs a lot of involvement and because the proper calibration of the of the heating freezing system the and also when it comes to the micro analytical or the analytical analysis of the fluid inclusions, when it is a very tedious or time consuming process like a bulk analysis by cross leach method. And then it needs one to understand the analytical details of what is how, what analytical method to go for like cross leach can be analyze by a ion chromatograph for it is concentration of the different anions and cations. And we have seen that there yet not a very single analytical protocol available where all the cations and anions could be analyzed.

And sometimes it is the use of instruments like an ICPMS which is advisable where the leachate also could be analyzed when they are present in smaller concentrations in part was parts per billion. So, it all depends on the instrumental methods is availability. So, even the simple analytical method like cross leach technique also could give very useful results in terms of the characteristic of the fluid.

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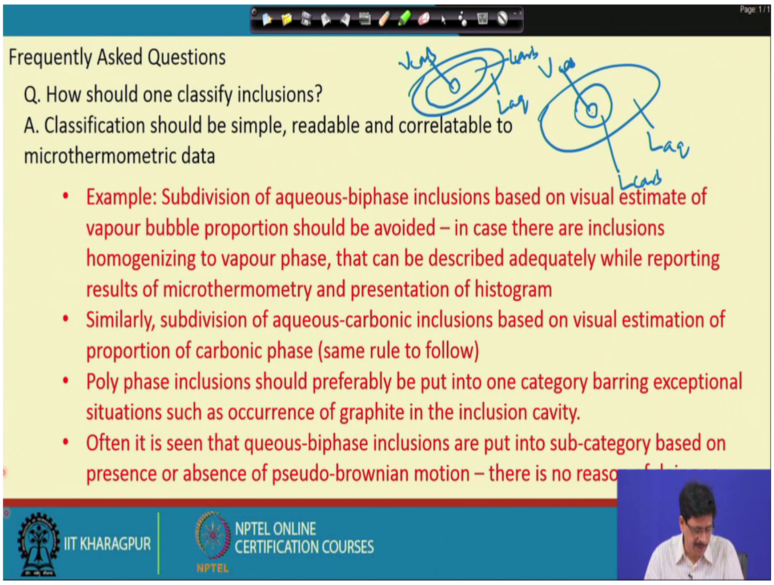

Frequently Asked Questions

Q. How should one classify inclusions?

A. Classification should be simple, readable and correlatable to microthermometric data

- Example: Subdivision of aqueous-biphase inclusions based on visual estimate of vapour bubble proportion should be avoided – in case there are inclusions homogenizing to vapour phase, that can be described adequately while reporting results of microthermometry and presentation of histogram
- Similarly, subdivision of aqueous-carbonic inclusions based on visual estimation of proportion of carbonic phase (same rule to follow)
- Poly phase inclusions should preferably be put into one category barring exceptional situations such as occurrence of graphite in the inclusion cavity.
- Often it is seen that queous-biphase inclusions are put into sub-category based on presence or absence of pseudo-brownian motion – there is no reaso

Now, we would like to just browse through the review the topics the subject that we have covered in this particular lecture series through something which generally could be describe under something like a frequently asked questions. I understand that this frequently asked questions will not be exhaustive cannot be made exhaustive right at this moment, but these frequently asked questions have been formulated in consultation with the graduate students who are working and are using fluid inclusions for their research. And so, that we know that what are the questions that I might come to the mind of a student or a researcher who is beginning to adopt this particular technique to solve his problem.

So, the basic thing that comes to mind then how should one classify inclusions, because we see that the inclusions could broadly be compositionally divided into the aqueous fluid or the mixed aqueous carbonic fluid and we see in the aqueous fluid there could be a many different species of dissolved electrolytes. They could be chloride, they could be carbides, by carbonate, sulphate and there is basically no limitation or no end to what could be the different electrolytes species, but they could we all be going under the similar a simple classification that there aqueous inclusions. And we can have the carbonic inclusions where the carbon dioxide is the dominant component.

And you could have species like methane, organ, nitrogen, or H 2 S and the other suffer bearing gaseous species, which remain miscible and when they represent in the inclusion their concentration is a variable rangers. And sometimes they are only suspected from the freezing behavior the temperature different temperature at which the phase changes are taking place. And say for example, like the critical temperature being elevated critical temperature of carbon dioxide instead of 31.1 it might go to a higher value of say 30 or even more and sometimes we ascribe it to the presence of H 2 S whose critical temperature is more or if it is the critical temperature is less than there are other species like methane and other species which could be presented.

Now, the so, then it should it could make one. So, one sees the classification when inclusion in a particular sample and thinking that there are both aqueous and mixed type of inclusions present, then we go for a classification of the inclusions to different types from my experience I would only suggest and share that the classification when someone is doing a petrography and is attempting to document or in the for the documentation wants want to classify the inclusions.

Then the classification should be simple, readable and correlatable to micro thermometric data. In a sometimes by making the classification complicated it also loses it is correlatability to the micro thermometric data that is generated and also it becomes at difficult to read for any person who is flowing the work.

For example, you will find sometimes in literature that the fluid inclusions aqueous inclusions are being divided into different types a b c d depending on just 10 percent, 20 percent, 30 percent or 50 percent of vapor proportion of the vapor that is present and as I have emphasize on this point that visual estimation of the vapor bubble the vapour in an aqueous inclusion is very misleading and erroneous.

So, subdivision of aqueous - biphase inclusions based on visual estimation of vapor bubble proportion should be avoided and in case there are inclusions. So, the only thing that is possible in an aqueous inclusion where the vapour bubble proportion is variable the only one thing that could be possible that those inclusions could be vapor reach and homozinsing into vapor phase. So, if we are classifying them only into the one type let us say we say that aqueous -biphase liquid plus vapor as our type one let us say.

Then when we find that many of the type one inclusions are actually homozinsing into vapor phase that can be very well the documented as the results of micro thermometry and that does not need to specifically the sub classified into a vapor region, liquid region inclusions. And so, they can be described adequately while reporting results of micro thermometry and presentation and also as we saw before that when we are supposed the sample is only having aqueous - biphase inclusion.

And we have completed the micro thermometric acquisition of the data and we are going to present the data and some of the inclusions on a good population of inclusions coexisting with liquid reach inclusions also homogenized into vapour phase. So, on the histogram we can represent them in different lazent or different kind of symbol or as we show before the sum of the histograms could be just put on the reverse side of the horizontal axis. And, can be represented as homogenizing into liquid as well as vapour and those diagrams could be better readable because if those kind of homogenization take place at the similar pressure temperature ranges, then the interpretation towards boiling fluid becomes more-more definite.

Similarly, the subdivision of aqueous carbonic inclusions based on visual estimation of the proportional carbonic phase also is sometimes done, that the carbonic liquid when there are presents to liquid. Say for example, there is a one in one inclusion aqueous carbonic inclusion where this is the L aqueous, this is the L carbonic and this is the V carbonic and suppose there is another inclusion which is over here, which is here and which is a L aqueous, this is L carbonic and this is V carbonic.

So, it may so, happened that usually these 2 inclusions are having different proportions of the carbonic and the aqueous liquid. And this variation could possibly be very gradational and this how variation again also is available to the problem of the geometry of the inclusion and the uncertainty of the third dimension and by just visually trying to estimate the proportion of the carbonic liquid part would be misleading.

So, again it is only from my experience and the suggestion that I could make here, that similarly the subdivision of the aqueous carbonic inclusions based on visual estimation of the proportion of carbonic phase should also we will so, also be avoided and they can be simply put into one category that the aqueous carbonic L, aqueous plus L carbonic plus or minus V carbonic as one particular type.

Now, similarly if they also do exhibit different modes of homogenization, one suppose there are 2 coexisting aqueous carbonic inclusion one is humanizing to aqueous comes through the phase and the other one is homogenizing to carbonic phase. These also could be very well recorded and documented while reporting the micro thermometric result. And we know that they do also have very important implications as for as the entrapment conditions of these particular aqueous carbonic inclusions are concerned.

Often it is seen that aqueous biphase inclusions are put into subcategory based on presence or absence of pseudo - Brownian motion, I find no reason in making any subdivision of aqueous biphase inclusions, based on the whether there is pseudo-brownian movement being executed in some and not in some other. Because it is purely I mean a situation in which it has got no relevance to the compositional characteristic or the entrapment condition or the nature.

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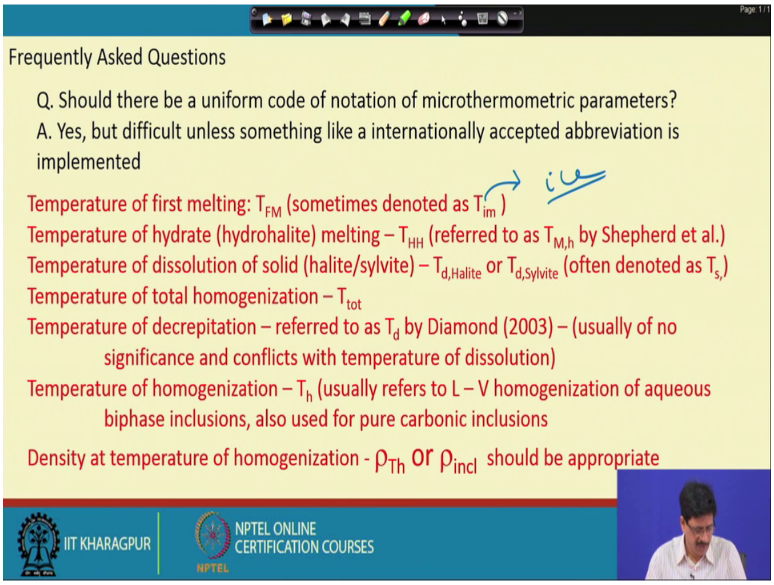

Frequently Asked Questions

Q. Should there be a uniform code of notation of microthermometric parameters?
A. Yes, but difficult unless something like a internationally accepted abbreviation is implemented

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Temperature of first melting: T_{FM} (sometimes denoted as T_{im})
Temperature of hydrate (hydrohalite) melting – T_{HH} (referred to as $T_{M,h}$ by Shepherd et al.)
Temperature of dissolution of solid (halite/sylvite) – $T_{d,Halite}$ or $T_{d,Sylvite}$ (often denoted as $T_{s,}$)
Temperature of total homogenization – T_{tot}
Temperature of decrepitation – referred to as T_d by Diamond (2003) – (usually of no significance and conflicts with temperature of dissolution)
Temperature of homogenization – T_h (usually refers to L – V homogenization of aqueous biphase inclusions, also used for pure carbonic inclusions
Density at temperature of homogenization - ρ_{Th} or ρ_{incl} should be appropriate

And there is also sometimes one issue which usually comes up that we are reporting the different micro thermometric parameters should there be a uniformity in that like for example, the mineral abbreviations are accepted or there as has been agreed upon by the some kind of an international convention; that this particular abbreviation should be used whenever the reporting of the done in reporting of them is between than in any scientific publication.

So, should there be a uniform code of notation of micro thermometric parameters the answer could be yes. But the difficulty lies and that some kind of an agreement has to be melt or internationally acceptable abbreviations has to be implemented for that. And as of now there is no such agreement whose been there. So, that is where sometimes some kind of mismatch is observed. And, the most of the notations that I have made during the course of this discussion is based on the book of the Shepherd Rankin and Alderton and on the Practical Guide to Fluid Inclusions. And, the different types of phase changes the temperature is corresponding into phase changes have been referred in the particular book.

For example, the temperature of first melting is represented as T FM and sometimes you will find that this particular temperature is being referred to is T im at that seems to be a little problematic, because i could also stand for ice. Therefore, the representing the temperature of first melting as T FM will be much more logical then referring to the particular temperature is temperature of temp T im. The temperature of height weight or the hydro halite generally we are talking we have only discussed about only particular one hydrate that is the hydro halite, the other one is the antarcticite which is the CaCl2.

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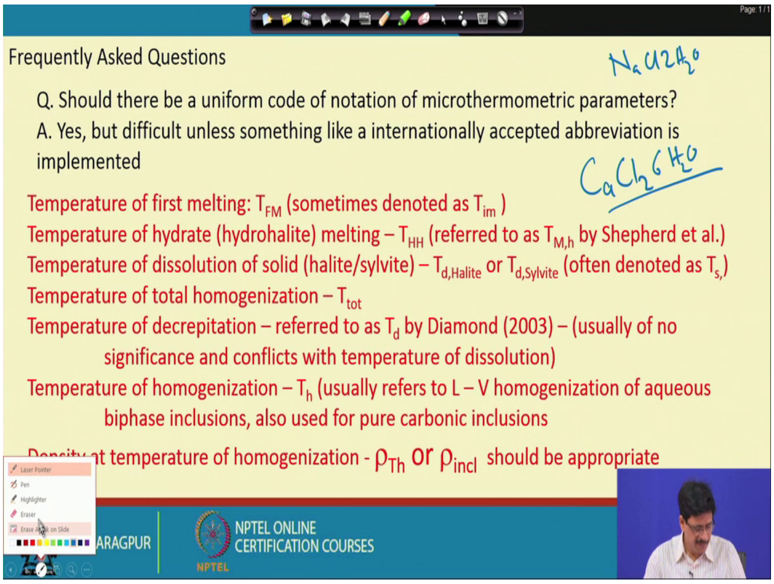

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$NaCl\,2H_2O$

$CaCl_2\,6H_2O$

C a Cl 2 6 H 2 O this is the antarcticite and Na C l 2 H 2 O which is hydro halite so, these are the 2 halites 2 hydrates that we have discussed mentioned. So, whether we should have what notation for the temperature of hydro halite melting; we generally use the T HH which refers to temperature of hydro halite. And, in the book of Shepherd et al it is it mean T Mh h for hydrate; that means, temperature of melting of hydrate.

Similarly, the temperature of dissolution of any of the daughter crystal like say halite or sylvite of for that matter any other mineral which could possibly be dissolve on heating. So, far we could see only these 2 mineral daughter crystal which actually dissolved and rest of them do not because of kinetic factors or maybe some other reason as it not understood.

So, we represent as T d halite or T d sylvite, d standing for dissolution in some cases some literature you will observe that this is being referred to is T s as temperature of solution, but generally it would be preferred that it should be represented is T d. And the temperature of total homogenization in case of a aqueous carbon inclusion is T total is mostly used by almost all the majority of the publications.

These are the things which are being discussed because the reading that has to be made by a person who is doing a fluid inclusion work by referring to many books. And, also in the context I would also like to mentioned that in addition to the book of the Shepherd Rankin and Alderton that was published way back in 1985 Blackie and I have no idea about whether this any later edition is available.

The other one which was a compilation of which was a monograph written by Edwin Rider published as one special one volume in the revision mineralogy in 1984 as Fluid Inclusions. And, it is essentially a massive compilation of all the work that was done by Edwin Rider it is geological US geological survey and where most of the things and when the fluid inclusion characteristics in different types of geological environment have been discussed very elaborately. I have not intentionally made reference to that particular compilation.

Because, for a beginner it may be bit difficult, but definitely that remains is one of the publication which has to be referred to one to get to make some better understanding and see many such a case studies has been described for the application of fluid inclusions. So, temperature at sometimes as we have discussed that in an aqueous carbonic inclusion while attempting to homogenized instead of homogenizing the inclusion gets leaked or decrepitated.

So, we discriminate we distinguish between the two terms decrepitation and leakages, decrepitation is a complete the escape of the content from the inclusion where the inclusion content is totally escape. Or in case of leakage we see that just the inclusion has deform by a little bit of a fracturing bit deformation and their content little bit of a content is has gone out from the main inclusion as just has been enrapt as a satellite inclusion somewhere nearby which I have also shown a diagrammatically before.

So, temperature of decrepitation for an aqueous carbonic inclusion is sometimes reported, but as we know that it is of no value because as does not give us anything, no of volumetric property or not more important conclusion can be made from that. Sometimes it is told that these temperature of decrepitation could be a very close approximation to temperature of a homogenization, if the inclusion is actually tending to homogenized by and at the time when the when you are one of the compound either the aqueous component or the carbonic component has reduced in the size considerably and is just on the verge of homogenizing; if it that point the temperature is inclusion is decrepitating then it possibly could make some sense.

But it is not usually true and so, in that case we only take it as a temperature of total homogenization, but then temperature denoting the temperature of decrepitation is T d will definitely conflict if you are representing T d as the dissolution, but they it is the used by some author, some workers. Then the temperature of homogenization is universally use as T h temperature of homogenization usually refers to as temperature of liquid vapor homogenization of aqueous-biphase inclusion or also pure carbonic inclusion. Sometimes we used for a parcel homogenization that we use T h carb.

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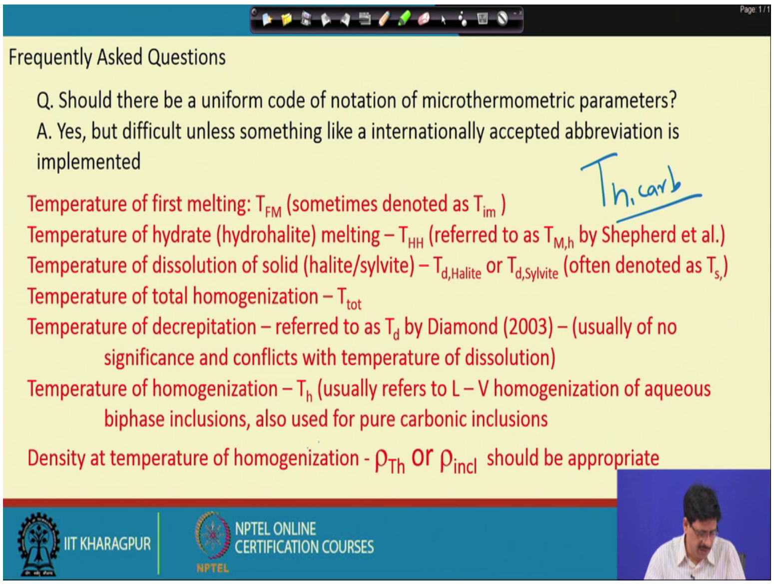

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Like, we put temperature of homogenization T h carb to refer to the parcel homogenization of the carbonic phase in a mixed aqueous carbonic inclusion. And, then the density which is represented as rho and generally this density we always mean when the inclusion is being homogeneous. So, whether it is the temperature of a homogenization liquid vapor homogenization or the temperature at which daughter crystal is dissolved T d or the temperature of total homogenization of a aqueous carbonic inclusion. So, the density which is rho is essentially referring to the density of a homogenous inclusion. So, density of the temperature of homogenization we always has a rho T h or as rho inclusion.

Because, rho inclusion sometimes would give you a better idea that yes, that is the density which we were talking about the homogenize fluid that is the inclusion. So, we continue in the next class about discussing about these frequently asked questions as for as fluid inclusion study is concerned.

Thank you.