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

Lecture – 16 Pure Carbonic Inclusion

Welcome to the lecture series, and we are in our 4th week of the lecture series. And we concluded discussing on the aqueous inclusions, but as we know that crustal fluid also I mean the water in the crust is charged with substantial other (Refer Time: 00:36) species like carbon dioxide, methane, nitrogen and argon.

The most dominant of which is carbon dioxide. And the carbon dioxide has a very limited solubility in water. And the solubility is a function of temperature pressure and also as we discussed before the visual solid in the aqueous phase.

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So, we will discuss about the simple case of the pure carbon dioxide. Because we see them occurring as pure carbonic inclusions in many rocks. In all almost all the types of rocks we study, whenever we go and see a an ore body a base metal sulphide in a gold or in a metamorphic rock and hydrate metamorphic rock we see this kind of pure carbonic inclusions, pure carbon liquid or carbonic vapor inclusions occurring in them. So, we will just try to see their response to freezing and heating. And just we will quickly recapitulate the entrapment condition of this pure carbonic inclusions. So, this is the phase diagram of a pure carbon dioxide unary phase diagram. The solid liquid line boundaries not shown here, but the difference is that with water here the d P by d T slope for solid liquid transition is actually as a positive slope because carbon dioxide decreases in volume on solidification, unlike water which expands on solidification twice.

Since that is on a very low temperature pressure design and we know that carbon dioxide is called dry ice, because the temperature corresponding to a atmospheric pressure which is about minus 76 degree Celsius does not have any liquid coexisting. So, it is actually vapor plus solid and that is why carbon dioxide is called as dry ice.

And we in the pressure temperatures diagram in this space, we recapitulate we discussed about entrapment conditions of this carbonic liquid that can give rise to a different situations of either a mono phase carbon dioxide liquid or a biphase. So, biphase means it is a vapor carbon dioxide and the surrounding part is liquid and the meniscus between the liquid and vapor is rather sharp with unlike what happens in a aqueous into then when it has a surrounded by a dark pin.

Let us considered that there are 2 packet of carbonate fluid or 2 inclusions which are trapped corresponding to situation 1 and 2. And this star corresponds to the room temperature condition and the pressure is defined by the vapor pressure of carbon dioxide on this particular curve. And we know this critical point of carbon dioxide corresponding to a pressure over 76 bars.

So, here if this inclusion evolves down it is isochoric path and then by the and the time at which it intersects the boiling curve a vapor phase nucleates and that is how at point corresponding to this star. We see them as occurring as liquid plus vapor biphase inclusion.

If this particular inclusion is again evolving, but it is correspond corresponding to the temperature, where it is a room rep temperature here corresponding to the star, it will be somewhere here, at a little higher pressure than the one. And it has not been able to intersected boiling curve. So, that is why it will present in the liquid curve liquid carbonic inclusion.

Here in this 3 diagrams are actually just for demonstration. So, these are very good examples. Here you see is a pure carbonic inclusions, a primary pure carbonic inclusion which has a very large dark vapor here. This is in a sample of quartz from one of the localities in India south India. So, here I have just shown that this part is the liquid carbon dioxide part and on solid on freezing corresponding to a temperature or it is minus 90 or minus 100 because of the super cooling this part which is now is being shown as a bright white part is a solid carbon dioxide.

And then this particular inclusion is shown in it is homogenous form. Because as we could if you compare these 2 diagrams you could clearly see that this particular dark vapor part has increased in it is volume and expanded and has filled up the whole cavity.

Like the situation which we described for discussed for your for the vapor rich aqueous inclusion determining the temperature of homogenization for vapor is carbon dioxide is also involves little bit of uncertainty. Provided the clarity the inclusions geometry such that the clarity is very good and we can get a we will not be having introducing much of uncertainty in determining the temperature of homogenization of a vapor rich carbonic inclusion where the homogenization is 2 vapor.

So, in this also the respond to freezing is also can be is also seen clearly here. Like exactly the same thing happens, if we have anywhere on the temperature any temperature then we should be getting the carbon dioxide to become solid it by less 56.6 corresponding to the triple point. But this does not happen it requires super cooling to variable degree sometimes you can go to minus 90 minus 95 or minus 100 and as exactly at the time the vapor bubble, changes it is shape as we know that it will evolve the solid will not it will be another less in volume compared to the liquid. But the vapor bubble will visibly will alter it is shape to accommodate for the solidification of the liquid part.

And we have to warm the reverse cycle of slowly warming. And when we warm at a controlled rate of warming is we discussed before could be 0.5 degree centigrade per minute or even sometimes even less to for a very precise recording of this particular temperature. So, if it happens to be a pure carbon dioxide this solid will melt at minus 56.6.

And then it will be again a liquid plus vapor situation. If we increase the temperature if it happens to be a liquid rich inclusion like this, then this will homogenize to liquid by disappearance of vapor.

And if it happens to be a situation like this, then it will be like an inclusion with a large vapor then it will be 2 vapor phase. So, that also we will take place either I mean less than or equal to 31.1 degree Celsius corresponding to the critical point of carbon dioxide.

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So now the situation is that this diagram depicts the density of carbon dioxide. This curve which has a parabolic path like this. This point corresponding to the this point corresponds to temperature of the critical temperature carbon dioxide just 31.1 and this is a critical density of 0.468 gram per cc

The depression the temperature as we know that a carbon dioxide carbonic inclusion carbonic liquid inclusion can homogenized. At temperatures either 31 point starting from 31.1 to any lower temperature corresponding to the triple point it is minus 56.6 and which is shown here up to minus 16.

So, as we go on if the carbonic inclusion above is homogenizing in at lower and lower and lower temperature means a density is higher going from the critical density value of 0.468 to any higher value. So, we will go discuss some of the situations in which the density what high value density value that we get in case of the carbonic inclusion. And this part of the curve corresponds to L plus V equal to L that is the liquid phase homogenization. And this part corresponds to L plus V to V what we just discussed. Here, as the temperature of homogenization goes on decreasing the density actually falls and it could be it falls off from the critical density of 0.468 to any lower values if the temperature is much lower.

So, this depends on the mode of homogenization. So now, here we definitely need to have some equation formulated to calculate so, we are also interested in getting the density value of the liquid carbon liquid carbonic inclusion or the vapor carbonic inclusion. Because density because it is a important volumetric parameter for us to know to characterize the crustal fluid. So, here also we have been looking for a formulation to calculate the density of the carbonic liquid.

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So, this kind of equations have been given in standard literature you will see, of the density is actually fitted with a 3 3 coefficient parameter here as we see here. So, it is a T by T c; T c is the temperature of critical temperature of carbon dioxide it is a 31.04 degrees' Kelvin. So, these are in Kelvin and the C 0 and C 1 C 2 parameter are empirically fitted to the densities to the volumetric data of carbon dioxide.

And from this expression it will be. So, d c density d c is the critical density of carbon dioxide which is known and with this parameter known with C 0 C 1 and C 3 parameter

known and the temperature is the temperature at which the liquid vapor homogenization is taken place capital T here corresponds to the temperature of homogenization.

So, through this equation it will be you can easily calculate the density it is possible these densities givens in centimeter cube per the densities given in grams per mole. So, it can be easily converted to grams per cc and in this case this is nature of the equation is also same, but only the parameters D 0 and D 1 and D 2 are different and here it is the density of the gas.

So, these are the kind of parameters which can be easily calculated by the in a simple excel spreadsheet or could be any other I mean writing a code or simply excel sheet could to be enough for calculation.

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So, now we come to the situation exactly that we discuss that a carbonic liquid or a carbonic vapor it is homogenization and we have determine the density. So, we also would like to calculate the constant of the isochore. How do we calculate the isochore for a carbonic liquid? So, we can we know that the actual situation here is not an ideal case.

We could possibly go for an ideal gas where PV is equal to RT for 1 mole of gas and there knowing R and knowing T you can always calculate pressure at any value of temperature, but we know that there situations correspond to very low pressure and sorry very high pressure and low temperature. And in this case the gas is to the real gas and this we know is the familiar Van der Waal's correction to the for the non-ideality of the gas, where it involves the excluded volume parameter which is b and the pressure correction term which is a. And this kind of equation could be used.

There are many other types of empirical feed like the virile equations which can also be used, but this parameter if you when worked out also can be utilized effectively for calculation of the isochore.

So, in from this very simple equation we know that we can calculate dp by dt and can see how it comes out to V. So, in most of the cases they do not look to be very (Refer Time: 13:05). So, in this case the dp by dt it is almost like a linear relationship to between pressure and temperature. So, we could expect that the isochore for a carbonic liquid also to be linear.

So, if requests asked for a pure gas to have the value of a and b are known, we know that this parameter b is considered to be independent of temperature and pressure. So, this could be a fixed value for gases like any of the gas that can be considered like water or carbon dioxide or methane.

Similarly, the a term is initially was taken to be a term which is an independent of temperature and pressure and was related to the critical temperature by this kind of an equation which is coming from the theory of corresponding states. But later on it was observe this particular a parameter by taking them is fixed values are not represent nor the producing the experimental volumetric data.

So, it was later on corrected with that this a is a function of temperature. And it was fitted a at is a 0 is a constant plus a temperature of function which can be empirically fitted is a 2 or 3 coefficient maybe a second or third degree equation in temperature.

So, this is the Redlich Kwong equation, where the additional the term was introduced and by which we could see that if we use this equation there could be a little bit of a deviation from linearity when we take the dp by dt slope, but that does not affect the results much. So, here the difference between the Redlich Kwong and the modified Redlich Kwong equation is that this a parameter has been fitted as a function of temperature and the b is still taken as independent of temperature and pressure. So, these are going through very simple formulations not getting in to the much of the elaborate of the much of intricacies into the this kind of formulations. So, here once we have the values of the temperature dependent functions for carbon dioxide known, then we can put the value here and also the b value known we can calculate pressure like before.

So or any particular isochore of carbon dioxide. So, if we have the inclusion homogenizing here, and we can use this equation modified Redlich Kwong equation where you can work out the parameter a and b is known b is taken from literature. And we can calculate a pressure at different temperature and can construct the isochore. We will see the utility of this isochores, but it is essential that we construct the isochores of this inclusions.

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Now, we know that this carbonic fluid inclusion that we see in many situations, many geological situations are very common and they are more common in situations corresponding to a metamorphic environment. There the also in metamorphosing fluid where there are mineralization resulting from such kind of metamorphosing fluid.

Where the carbon dioxide is having variable concentration of methane in it and since methane and carbon dioxide a completely miscible in all proportions and also is shown before. You can have a continuous critical curve between the critical point of carbon dioxide and critical point of methane. Critical point of methane is around minus 82 degree Celsius whereas, that of carbon dioxide is 31.1.

So, now the situation is that if we have some concentration of methane in a carbonic inclusion what happens to it. From the standard curve that we saw before, if methane will depress the triple point of carbon dioxide. So, if we have an inclusion where the temperature and melting of solid carbon dioxide is depressed from value which is which from 56.6 degrees Celsius which is the pure for pure carbon dioxide here. So, minus 56.6 is the value for the pure carbon dioxide. Then we know that this carbon dioxide is not pure it contains methane.

So, depending on what is the mole percent of methane the value could be any lower than minus 56.6. Theoretically you can go to minus 182 which is a triple point of methane, but we generally get methane concentrations going to range of minus sorry 0.5 0.6 mole fraction. So, we can always consider under such kind of compositional ranges composition.

So, here so, the situation is that similarly if the carbonic liquid also contains methane, the homogenization temperature is also depressed, but then since they have a common critical curve. So, this similarly the temperature of homogenization of the of the inclusion will not be corresponding to the boiling curve of either of them, but some kind of a curve which will be joining between we carbon dioxide and methane corresponding to that particular mole fraction of methane.

So, then there are presently available direct methods in situ non destructive analysis of the inclusion fluid, my spectroscopic method like Raman spectrometry which we will be discussing. But if in the absence of such kind of a facility or such instrument for measurement for direct in situ non destructive analysis of the inclusion fluid.

One can still calculate approximately the mole percent of methane. Either can be repressive explicit is mole percent or mole fraction. So, this diagram which is on the left is a overall situations in which the mole percent the molar volume of a carbonic fluid will change with very mole percent of methane.

So, the mole percent goes on increasing with the molar volume with increasing. And this line this dotted line actually separates between the 2 domains where it is mostly as we as

you can see the molar volume is going to very high value. So, this is with the vapor part and the molar volume below the critical volume will always be the liquid rich region.

So, this diagram which is on the right is enlarged to a part like this somewhere here, moving up to mole percent of methane of about 30. And here we see the situation in which the solid curves here are the curves representing situations of homogenization of the carbonic inclusion and liquid vapor inclusion. And see the temperature 20 15 10 5 0 minus 5 minus 10 minus 15 and so.

So, this will be the iso th line this curves iso th curve for that particular carbon dioxide. The thin lines are the melting temperature of carbon dioxide, which we know that for a pure carbon dioxide it will be minus 56.6 it can go down in the to low any lower temperature. So, these are the. So, this is also correspond to the mole percent of methane. So, we see that we could see here clearly that the mole percent increases means the solid carbon dioxide melting is depressed to variable degree with the increasing in mole percent is goes on decreasing to minus 60 or even much lower values.

So, this is it has been devised that the mole percent of carbon dioxide, mole percent of methane in a carbonic liquid can be measured can be estimated or reduced from the intersection of the curves representing these iso homogenization temperature with that of the melting temperature of carbon dioxide.

For example, if we get a temperature of homogenization of 20 degrees Celsius and the temperature depression in freezing point depression in melting of solid carbon dioxide to around minus 57 point something, then we can calculate that it could have a value of the methane mole percent to be something between 5 mole percent or so. This diagram could be further resolved and exactly could be very well extrapolated. And this is this particular diagram on the right corresponds to the liquid region; that means, the homogenization is from is with that mode of L plus V to L and there is depression in melting temperature of cartoon dioxide from minus 56. So, then we can once we determine both and it is we can easily calculate what is the percentage of methane.

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So, this one is in the vapor rich domain. So, here the molar volume is going to 400 even or more than that like before this is 50.6 line where corresponding to pure carbon dioxide. These are the lines corresponding to the depression in this melting of solid carbon dioxide. And these are the curves corresponding to 25, 20 and go on up to minus 5 minus 10 minus 15 even.

So, as you can understand this cut this could this could be drawn for a complete range of consideration from 0 to ah; that means, pure carbon dioxide to pure methane this kind of diagram can be constructed at they are available. They may there are many workers we have done work on this system and have extended this and write at this moment without the help of precise analytical equipment like laser Raman micro laser Raman spectrometer where you can do an in situ non destructive analysis.

And can calculate the percentage mole percent or mole fraction of methane in the carbonic liquid. We know that also once the solid carbon dioxide melting temperature and homogenization temperature are precisely determine one can always calculate the methane percentage in terms of mole percent or mole fraction.

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Density of CO_2 -CH ₄ Inclusions O_2 -CH ₄ Inclu	Shiring Con
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Well; so, then the situation here is that, if we the equations that we described for determination of density of carbonic liquid there we took that equation to be of the pure carbon dioxide without considering any methane.

So, if we have to calculate the density of a carbon dioxide liquid and also intern the isochore, then it is essential that we should work out the formula we must know how to calculate the density when there is variable concentrations of methane.

So, again go which we again revoke the same equation substrate like our modified Redlich Kwong equation which is which is actually P is equal to RT by V minus b minus a by V into v plus b T to the power half. So, here these a and b terms will no longer be of the pure, but the end b term will be of the mixture.

So, we have to we know that what is the mixing rule, we will discuss them in the subsequent classes, but there is definitely this for the a term the pure the for a mixer like carbon dioxide methane they have to be known how to use the mixing rule that mixing rule could possibly the simple both b and a.

So, mixing rule will definitely be depending on the mole fraction of the carbon dioxide and methane. And also must be taking help of the values for pure components of them; that means, if we say that for a pure carbon dioxide we can say that it is a 0 and for a 0 carbon dioxide and for a pure carbon methane we could say that this is could be a 0 c H 4.

And similarly for b we will have fixed value of the methane as well as b of carbon dioxide and these are this must have been worked out and are available in literature in standard literature from empirical feet or from experimental determination.

So, but then we have to have this known, and we also must have the mixing rule something like we to put as that a of the mixture, should be equal to like the mole fraction of that particular sorry xi and xj, means the jth if we take it this 1 is for carbon dioxide and 2 for methane then we will can expand the term and can calculate which will be something like the a of the mixture and similarly b of mixture.

This is a simple rule bix I means the b of mixer will be b of methane into the mole fraction of methane plus b of carbon dioxide into mole percent of carbon dioxide. In this case here because of the double summation term we will get some cross term which will be which we will discuss later when we come to the aqueous carbonic inclusions.

So, this a and b parameters for ch 4 have to be known which are available in the literature. This modified Redlich Kwong equation has to be solved now once me when we were writing the MRK equation.

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This p is equal to RT by V minus b minus a to the power a by temperature to the power half and v plus b. We know that we can once we know the a and b parameter for any

particular pressure this particular equation can be solved from molar volume. Because this can be can be can be rearranged as a cubic equation in V.

So, the MRK equation can be solved for molar volume for a fluid mixture for a range of a pressure and methane. So now, what exactly I have just possibly elaborate a little bit of a methodology which I implemented.

So, what we can do in order to calculate the density of a carbon dioxide methane mixture, what we did is that we with the known value of the b that is the corrected the correction volume (Refer Time; 38:52) for both methane an carbon dioxide available and the a term also worked out the mixture mixed mixture term for the pressure correction which is a.

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Density of CO ₂ -CH ₄ Inclusions	
 Need a and b parameters for CH₄ (available in literature) Solve MRK equation for molar volume of fluid mixture for a range of Pressure and X_{CH4} and convert molar volume to density (g/cc) Regress density as function of Temperature and X_{CH4} (applicable to X_{CH4} of up to 0.3) 	
$\underbrace{\text{Density } (g/cc) = 0.38605 (\pm 0.04007) - 0.00742 (\pm 1.43042 \times 10^{\circ}) T(K) + 2.56322 (\pm 0.0356) X_{CO2}}_{CO2}$	
Isochore of CO ₂ -CH ₄ M R K Equation of State	

This a and b parameters with are available, with that the modified Redlich Kwong equation can be solved for molar volume at different values of pressure and mole fraction of methane. And that molar volume can be converted to density in terms of grams per cc because we can only this molar volume is cc per mole and it can be converted to mole per cc and mole can be converted to gram and can be converted to can be opted in form of grams or cc

Now, if we regress the density value do some empirical fitting of the density value that we obtain in this set of we can worked out for a huge for a complete range. So, we did it for applicable to X CH 4 going to 0.3 means 30 mole percent from pure carbon dioxide to 30 mole percent of methane we worked out and then fitted the regression equation to it like the one which is shown here.

And the regression the uncertainties are also shown here and this particular equation we can use for calculation of density of a methane and carbon dioxide mixture and is applicable only from a mole fraction of carbon dioxide from 0, sorry mole fraction of methane from 0 to 0.3.

Now, the what is the utility of this? Because as we know that if we neglect, suppose we measure the mole fraction of methane by using the standard intersections of the tm CO 2 and the th Co 2 curve as shown before. And then we do not take on saying do not take the methane to consideration well calculating the density then we will overestimate the density of the carbonic fluid to a great extent. Because of the simple reason that the temperature of homogenization of the carbon dioxide actually was depressed because of presence of methane.

Headed; so, headed been the case of a pure carbon dioxide we know that the lower and lowered the temperature homogenization is actually the fluid is actually denser and denser. So, then for example, if we consider will in a just for a sake of example, if we consider that a carbon dioxide carbonic liquid inclusion homogenized at 20 degrees Celsius.

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We can calculate the density of this particular 20 degree Celsius of carbon dioxide temperature liquid homogenization, let us say it comes to the 0.8.

Now, if this particular homogenization has taken place at 20 degree Celsius, but had X CH 4 of say 0.1 then this density would be reduced say for example, for a crude it may go out to 0.75 or even less. So, if we get a get a temperature of and now similarly. So, if we take that homogenization which is happening in much lower temperature at 0 or my negative temperature values. So, we will calculate densities of carbon dioxide which comes to be far more than what it actually is because the depression has been caused by the methane.

So, that is how this it has a very important implication that we must take into consideration the methane concentration while calculating the density of the carbonic liquid from the data on temperature of depression of the melting of carbon dioxide and the temperature of liquid vapor homogenization whether it is to liquid or to vapor.

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So, in this case this point the limitation right at this point of time that this particular equation is actually only applicable when the homogenization of the carbonic liquid carbonic inclusion is to liquid.

So, it needs to do be worked out or maybe there is some somewhere the some formulation is existing. So, one has to use equations which will be applicable to the vapor region or the vapor phase homogenization. So, you will conclude our discussion today with this and we will continue in the next class.

Thank you.