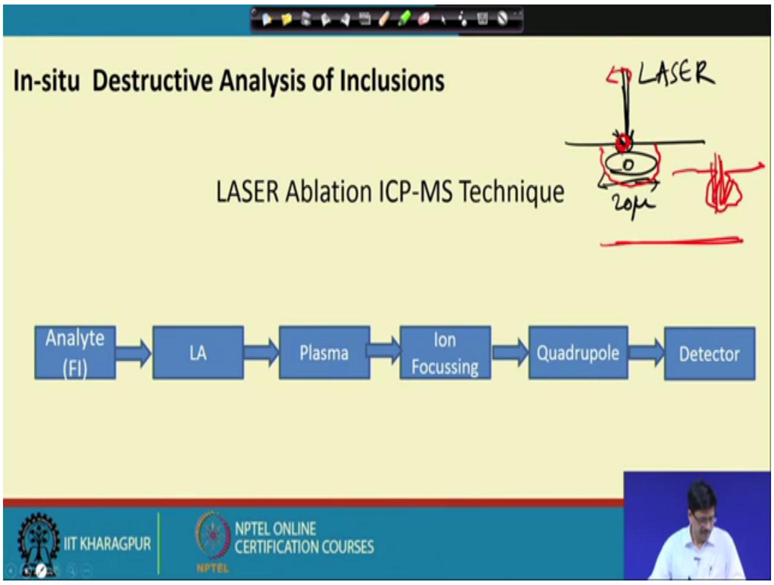
Fluid Inclusion in Minerals: Principles, Methodology, Practice and Application

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

Lecture – 35
Analysis of Fluid Inclusion (Contd.)

Welcome to today's lecture, we will continue our discussion on the in-situ non destructive analysis microanalysis of a fluid inclusions. Today we will discuss on some of the other techniques which are also adopted by scientists across many different laboratories in the world. To begin with there is another particular technique. So, we will go to from a non destructive to destructive technique.

(Refer Slide Time: 00:50)



In-situ Destructive Analysis of Inclusions

LASER Ablation ICP-MS Technique

Analyte (FI) → LA → Plasma → Ion Focussing → Quadrupole → Detector

This, the destructive technique essentially is that the inclusion content is taken out the inclusion is destroyed. So, one such in-situ destructive analytical technique is the laser ablation ICP MS it is Inductively Coupled Plasma Mass Spectrometer. We have already discuss the working principle in very brief about how a inductively coupled plasma mass spectrometer works.

It works with a bring into the material into a plasma state and then in a ionic state and the ions are actually for the carried guided through some lenses focus through some lenses which are essentially by applying proper current and voltage through the cones. And then through the ion lenses in particular and then, they are guided through a quadruple which are essentially 4 rods which are the alternating rods are having RF and the DC fields.

And appropriate combination we will make specific ions based on their mass base charger base charge by mass ratio to be guided through to be detected by detector. So, here the technique is used for fluid inclusions with a variation that it is actually. So, it is essentially called as dry analysis because, the inclusion content is for example, if there is an there is a vapor and in this vapor, there is an inclusion which is here at a depth of some microns.

And then, this is the laser when a closed chamber in absence of any other gases in a closed chamber. Again laser with a these laser is different from the laser which is used in l r n. This is pulse laser much higher in its energy excimer kind of laser or Nd YAG neodymium, yttrium, aluminum, garnet, kind of laser which have much higher in energy.

And this particular laser beam of a particular spots size, suppose this particular inclusion is measuring some 20 micron or so. And so, what will happen is as and when this laser keeps on getting the surface, the material here is will be the material here, because of the very high temperature the very high energy pleasure which is following which is will be generating a lots of temp high temperature. It will essentially, ablate or evaporate the material which will be just above the host mineral which is just above the inclusion. And with continued heating up that laser pulse laser on the on this particular spot it will ultimately reached the inclusion and by increasing the beam diameter of this particular laser.

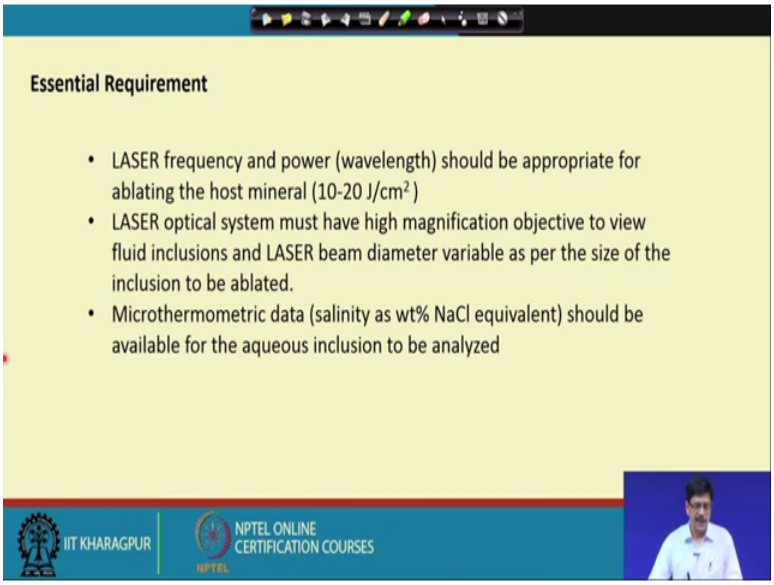
So, what we will get? We will get the entire this content to be taken out and essentially what will happen it is so, the initially this thing which was the surface of the vapor it will create a kind of a whole or a cater. Because, most of the inclusion content. And once they are solid host above the solid host here is ablated.

And the liquid part will very easily be ablate whatever is there liquid and gas will always be converted into will be evaporated nebulized and then it will be with the help of the career gas. So, it is written here the analyte is the fluid inclusion. So, this fluid inclusion which is situated in an solid mineral host and at a particular depth from the surface is gradually ablated and this material is carried by this career gas and then rest of the things is similar to what happens when LA in an ICP MS.

So, it goes to the so analyte it goes to the laser ablation it is ablated and then with the career gas. Then it comes to the plasma where it is converted to its ionic state and then the ion focusing on the quadruple and the detector. So, the only difference here is so, the only difference here is that when we have any particular solid surface like a mineral is being ablated for the analysis.

The mineral will for a particular for a longer period of time, whatever is being ablated or is taken by the career gas will be the same. Whereas, in case of fluid inclusion it will only be a where a very short time that the content of the inclusion will actually be going to the detector and what we get there?

(Refer Slide Time: 06:33)



Essential Requirement

- LASER frequency and power (wavelength) should be appropriate for ablating the host mineral (10-20 J/cm^2)
- LASER optical system must have high magnification objective to view fluid inclusions and LASER beam diameter variable as per the size of the inclusion to be ablated.
- Microthermometric data (salinity as wt% NaCl equivalent) should be available for the aqueous inclusion to be analyzed

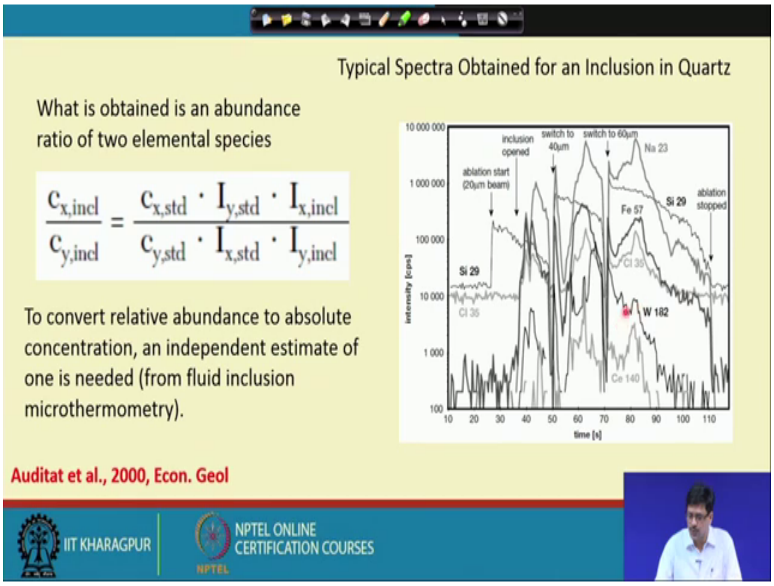
So, the essential requirement is that a laser frequency and power should be appropriate for ablating the host mineral, the energy is of the of the order of 10 to 10; 10-20, 20 joule per centimeter square. And the laser optical system must have high magnification because, these inclusions are timing in terms of tense of microns are even sometimes less than ten micron.

So, if you want to put the lasers for exactly on the inclusion, then we should be able to view the inclusion properly so, the laser of the microscope system which is couple to the measure ablation should have the proper magnification. So, laser optical system must have the high magnification objective to view fluid inclusions and laser beam diameters variable as per the size of the inclusion ablated. That because, we initially we start with a smaller diameter size of the laser to the laser spot, and then increase it to so that we would be getting the entire content of the inclusion to ablated and analyzed.

Now, micro thermometric data should be available for this aqueous inclusion to be analyzed. Here the situation is that it possible that we analyze the electrolytes in terms of the chlorides of the dominant cations like sodium potassium calcium magnesium ion and so on those are much more easily analyze.

Because, in these system the possibility that analyzing chlorine which would be requiring much higher there the ion anions potential is form of higher. So, even though it is not impossible to analyze, but it is far more easier to analyze this cations and rather than the anions.

(Refer Slide Time: 08:20)



Typical Spectra Obtained for an Inclusion in Quartz

What is obtained is an abundance ratio of two elemental species

$$\frac{c_{x,incl}}{c_{y,incl}} = \frac{c_{x,std} \cdot I_{y,std} \cdot I_{x,incl}}{c_{y,std} \cdot I_{x,std} \cdot I_{y,incl}}$$

To convert relative abundance to absolute concentration, an independent estimate of one is needed (from fluid inclusion microthermometry).

Auditat et al., 2000, Econ. Geol

So, the micro thermometric data should be available, because prior micro thermometric data where the salinity in weight percent equivalent should be available why is it here it is mentioned.

So, this diagram is a typical spectra which is obtained by a laser ablation of fluid inclusion here the intensity is plotted against time. So, we could see time in seconds from 10 to 110 seconds and what we could see here that are from beginning up to another 20 seconds are so, we are seeing the this is a silicon 50 which is being showing here silicon

29. And the time that is taken for the host mineral to get ablated and the inclusion cavity is exposed to the laser beam and the ablating starts here.

And then we see so, these are the different steps in which the laser beam so, it is initial it is a 20 micron beam it is a 40 micron beam up to 60 and as the laser spot size is increased. So, we are getting higher and higher signals of this elemental species, we could see with the chlorine 35 still can be analyzed.

And here the different elements peaks are shown here for example, this is tungsten, chlorine, this iron sodium, sodium peak we could see here sodium 23. And this only the time that we have that this peak it is actually taken from because, there is no laser ablation data on fluid inclusion any generated in house and these are as far the reference given here. So, this gives us a tip typically an idea actually what happens and the laser ablation kind of destructive analysis. So, it and after the inclusion cavities all and exhausted then again it comes back to the same host mineral spectra that would be a spectra. So, this kind of a so, it is very transient signals are transient.

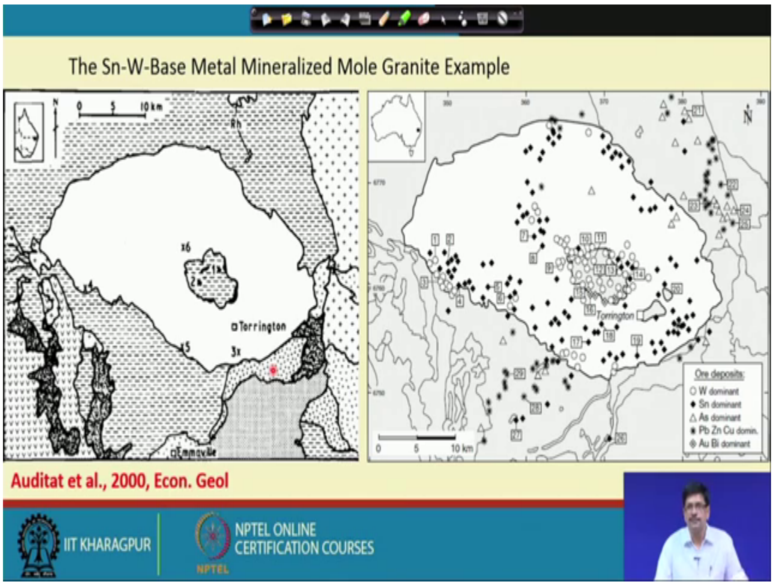
So, it leads very the data reduction has to be done very elaborate way which I will not be discussing here much what essentially we get if suppose; so, this is abundance ratio of the two elemental species from this kind of spectra. on a LA ICP MS. So, this can be expressed only in terms of that the concentration of x and concentration of y in the inclusion, will be a ratio of this concentration of x and concentration of y in the standard intensity of y and intensity of x in the standard and intensity of x and intensity of y in the inclusion.

Now, in you to convert to this relative abundance to absolute concentration an independent estimate is needed and that is coming from the fluid inclusion micro thermometric. So, still so far when till recently the LA ICP MS analysis to convert it to actual concentration in the inclusion species. It is always essential that it should be the prior micro thermometric data is available and some value for this weight percent N a C l equivalent; that means, in a way the sodium concentration is known. As you remember, when we were discussing about the ion chromatography and technique, and then we showed some relationship between what is exactly the total sodium chloride weight percent equivalent that will contributed by sodium that is 1.5 of magnesium and 1.5 of calcium and so on.

So, some such kind of a standardization procedure has to applied here and so, that a sodium concentration can be roped and that sodium concentration can be used as an intern internal, internal standard and the analysis to be done. So, that is the kind of what is happening at the right at this point of time till recently that there are some select. And this kind of facilities are there in many places and there are fluid inclusion is through work are specifically to understand the ore forming process.

So, that the concentration of different metallic species sometimes like for example, shown here tungsten, iron. And these example actually taken from the mole granite, again I will come back to the same mole granite, example which we discussed in context of the application to a deposits.

(Refer Slide Time: 12:36)



The Sn-W-Base Metal Mineralized Mole Granite Example

Auditat et al., 2000, Econ. Geol

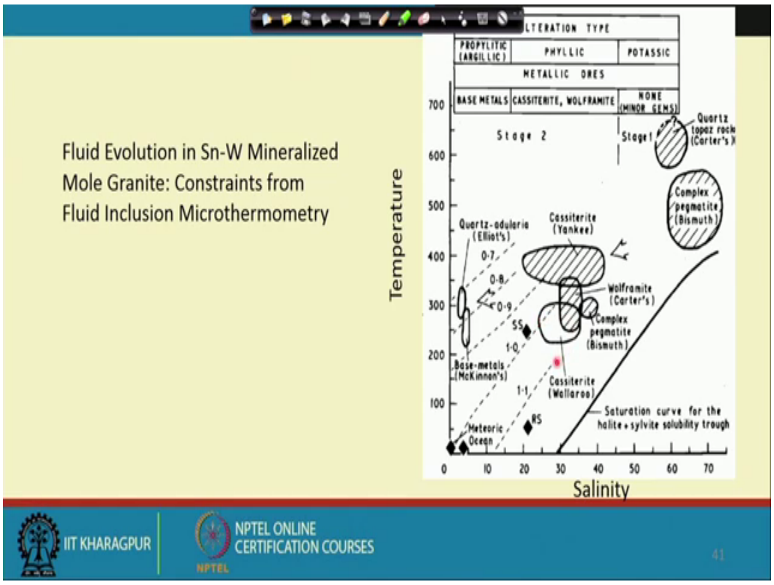
IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

If you remember we are talking about a situation where the mole granite at the New England, Batholitha and Eastern Australia is a classic example of mineralization of tin, tungsten and base metal.

Where, we have compare this is a map in which this part which is we show without any hatching is basically the mole granite and these are the metacidmetry country rock with some other granitic members present. And the mineral deposit distributions are like this with the white circles are all tungsten dominated, then this diamond tin and in the periphery we will see that the lead and zinc copper sulphide deposits.

(Refer Slide Time: 13:22)



Fluid Evolution in Sn-W Mineralized Mole Granite: Constraints from Fluid Inclusion Microthermometry

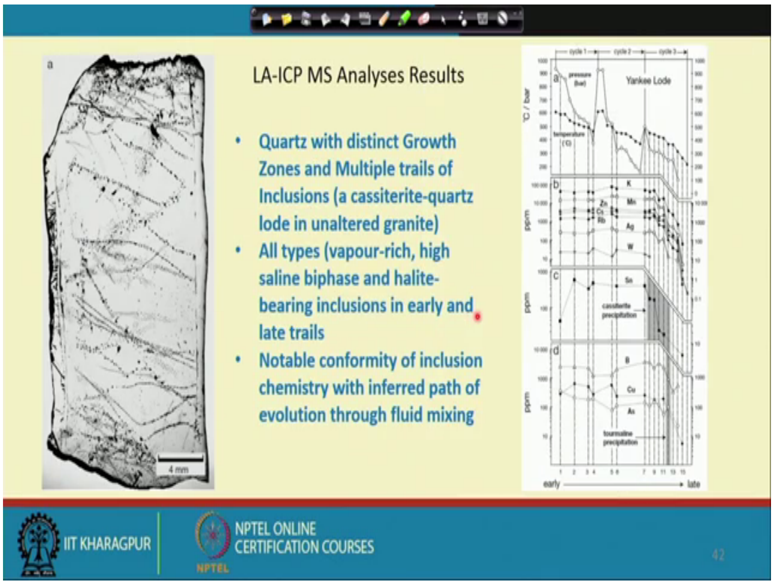
IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

And the just to recapitulate, then from fluid inclusion micro thermometric data from the salinity and temperature data the authors way back this is taken from old literature of the early 80’s with the difference which I get before. So, from fluid inclusion data itself the inclusions in to pass in the early phase of magnetic fluid where there was boiling.

And then, the complex pegmatite and then the tin quartz cassiterite rein in another granite and then giving rise to quartz cassiterite then in alter granite. And then finally, the led and zinc sulphide deposits. So, that kept there was a very good idea about the way the fluid evolve and present time with after the warning phase of the magnetic fluid activity with the boiling of the fluid after the boiling one down.

(Refer Slide Time: 14:28)



LA-ICP MS Analyses Results

- Quartz with distinct Growth Zones and Multiple trails of Inclusions (a cassiterite-quartz lode in unaltered granite)
- All types (vapour-rich, high saline biphase and halite-bearing inclusions in early and late trails
- Notable conformity of inclusion chemistry with inferred path of evolution through fluid mixing

So, then only gave rise to the scope for if meteoric fluid to mix with it. And it finally, ended up with the low temperature situation, low temperature, low salinity situation when the sulphides deposited. So, here the same mole granite example mole granite was and the mineralization was subjected to the LA ICP MS study shown in the reference before.

So, this is one example of one particular section are taken from a quartz cassiterite when, where the quartz this is you could see this is a polyester section of the quartz where the different generations of the trail bound inclusions are shown and it has got about 3 to 4 growth zones. And, when the several such generations of the trail bound inclusions which are supposed to be preserving the fluid characteristics in the complex path of evolution starting from very high salinity, very high temperature, where the temperatures then salinity from the fluid inclusion studies are also shown on the top here starting from 600 700 degrees Celsius temperature to going down to 200 degree Celsius temperature and this spectrum.

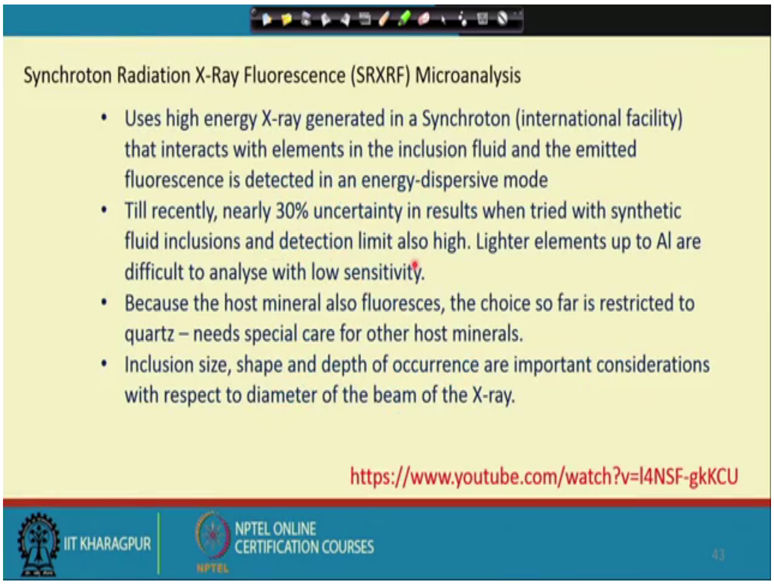
And this particular inclusions of different generations where subject where done subjected to this LA ICP MS analysis where you could see the potassium manganese, silver, tungsten, tin, boron, copper and arsenic these are the species which were analyzed. And we could clearly see that there are conditions or because the dictate the temperature and the salinity kind of situation in which most of the metals were held in solution there were transporting. And there were domains after the mixing of the temperature and salinity values decreased the fluid mixed with the meteoric fluid and then the deposition of the metals took place where the fluid inclusion so, very decreasing concentration of such kind of metals.

So, it is a notable the conformity of the inclusion chemistry with inferred path of the evolution of the fluid mixing is pretty, it is quite notable here. And here it is a so; so this a reason why it I chose this as a case study to be shown here, where there is a perfect agreement between what is actually inferred from a micro thermometric data and the fluid evolution. And then when the inclusions where analyzed by non by destructive in-situ domain and method like laser like laser of the LA ICP MS we get similar kind of picture.

This very it is also possible I mean this is just one such example that a many many such case studies of application of this technique into many other deposits where, inclusions are ablated and analyze from the ore minerals. As well as the silicate gang are associated with them and the difference in the fluid characters is also brought out and many very many very very important conclusions are arrived at as such kind of study.

So, there is no denied to the fact that the in-situ or the analytic the analysis of the inclusions need to be followed up after the fluid inclusion micro thermometric micro thermometric exercise to get better idea about the fluid characteristic, fluid chemistry evolution and so on.

(Refer Slide Time: 17:29)



Synchroton Radiation X-Ray Fluorescence (SRXRF) Microanalysis

- Uses high energy X-ray generated in a Synchroton (international facility) that interacts with elements in the inclusion fluid and the emitted fluorescence is detected in an energy-dispersive mode
- Till recently, nearly 30% uncertainty in results when tried with synthetic fluid inclusions and detection limit also high. Lighter elements up to Al are difficult to analyse with low sensitivity.
- Because the host mineral also fluoresces, the choice so far is restricted to quartz – needs special care for other host minerals.
- Inclusion size, shape and depth of occurrence are important considerations with respect to diameter of the beam of the X-ray.

https://www.youtube.com/watch?v=l4NSF-gkKCU

We will talk about again a method which is non destructive. Which is a method which is essentially the synchrotron source X-ray fluorescence or expense its also said synchrotron radiation X-ray fluorescence and it is mentioned SRXRF for ss it does matter. But actually it is come from a synchrotron, we all know that there are they can be only called as international facility because, their particle accelerator. And in order if want to if anyone wants to know more exactly right how exactly this synchrotron works this link I am providing here.

There could be many many such sources of knowledge in public domain about the synchrotron.That essentially accelerators in which this electron which are generated from the particular source. And made to move in a closed space at velocity is almost equal to the velocity of light.

And in the process gaining energy inter in the magnitude of the Giga electron volt and when this particular so the electron which keeps on accelerate in a in a closed space in a grain kind of thing in stainless steel. So, they this of electron they emit light intensity almost in a very very high intensity of light. And by using a proper magnetic field this particular radiations or this a can be deflected and can be depending on the requirement the. So, they are essentially sources of high intensity electromagnetic energy, we can choose the exactly wavelength range that we want.

Say for example, we know that an extra range will be a very suitable range for analysis of elements as you know conventionally by X-ray fluorescence techniques. Which we used for a in conventional X-ray, where the X-rays generated by an X-ray tube like a tungsten source are we all know when a energy which is almost about 4 kilo watt are so.

But can compared to that these are far more high energy system and that is why that there are possibly very limited number of non facilities all over the world in different parts of the country, different parts of the world. So, this should if we basically select the particular wave light of the particular wavelength which is in the extra range. And guide them as of the in a particular synchrotrons such some such multiple points, on which this higher energy on the electromagnetic radiations can be deflected.

And can for multiple sub stations are which are essentially the laboratory is in which this race could be utilized for various types of studies, every routinely used by physicist for study of material, material structure and so on. But this could be always, this could also be used for analyzing the fluid inclusions, some such results are reported although very few in number in literature.

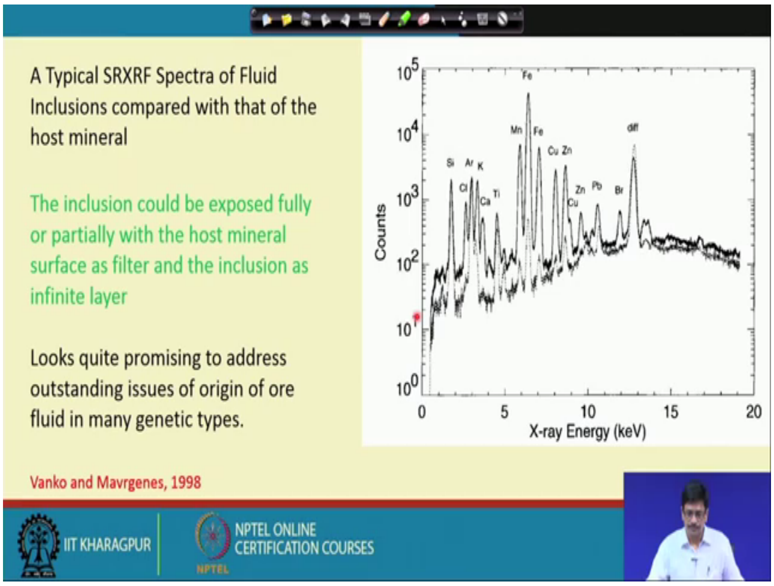
So, till recently nearly 30 percent uncertainty in results when tried with so, there are some work which were essentially tried by taking some synthetic fluid inclusion; so it known concentration. And then see how the signals are coming and these particular technique has a lot of I would say promise for addressing issues of for the for the fluid ore fluid, they concentration of the ore metals in different evolutionary path of fluid in any kind of a mineralizing system, like I say orogenic gold at deposit system or a magnetic or a power free copper system where, they are actually it could be utilized.

But then, till so far they the analytical protocol has not been very successful when it was tried with synthetic fluid inclusion for analysis of strontium it was observed that about the detection limit was about almost 2000 ppm. And whenever, and then another problem is that the elements up to aluminium analyzing them is not it will not is almost impossible, it is not a not so far been achieved with high precision and elements from silicon onwards it could to be analyzed with better precision.

And the another a situation is that since, many host minerals will also fluoresces to the X-ray the choice so, far as is been restricted to quartz and but then definitely more research will definitely make it suitable for other materials as well. The inclusion size, shape and the depth of occurrence are important considerations with respect to the diameter of the beam of the X-ray.

The diameter of the beam of the X-ray can be you variable depending on the inclusion size that one wants to analyze. So, exactly same they like this fluid inclusion is vapor could be taken as the sample on which it could be exposed to the synchrotron source X-ray, and then the fluorescence could be studied by using appropriate detector.

(Refer Slide Time: 22:56)



A Typical SRXRF Spectra of Fluid Inclusions compared with that of the host mineral

The inclusion could be exposed fully or partially with the host mineral surface as filter and the inclusion as infinite layer

Looks quite promising to address outstanding issues of origin of ore fluid in many genetic types.

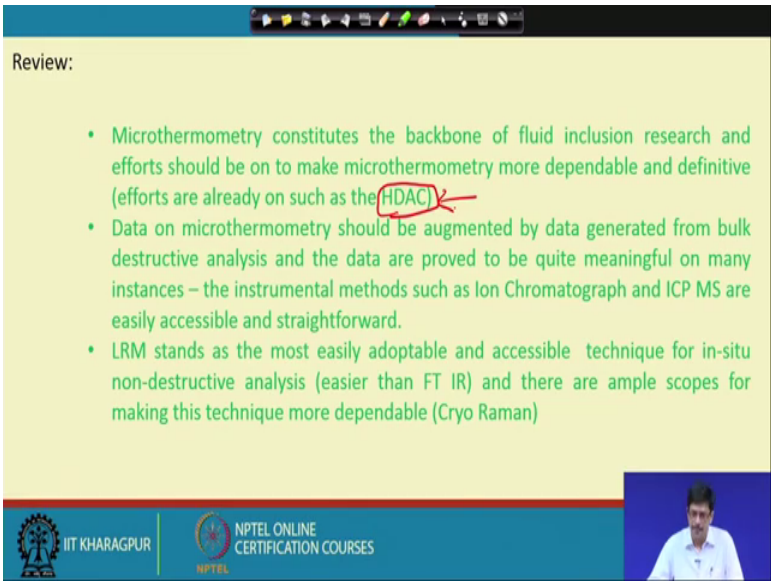
Vanko and Mavrgenes, 1998

This is one example of a an aspect to obtained from a synchrotron source extra fluorescence, this X-ray energy in kilo electron volt is given. And we could see that are this is the solid line is from the inclusion and the dotted lines for the source for the host mineral, where you could see the silicon peak is coinciding. So, it gives us the idea that yes, this analytical process is actually is consistent.

And then we could see that some of the signals are the elements like iron, manganese, copper, zinc, led as much higher corresponding to what the signal is obtained from the host mineral giving us a have an idea that this could be a very effective technique of analyzing. Or for example, in some of the cases where we have now, we still debate on which fluid actually was carrying the cold as we discussed before in case of the orogenic gold deposits. We still we still debate about the actual source are even in case of multiple sources of the ore fluid.

So, if they could be analyzed with the inclusions of particular that particular generation could be selected or those particular samples which represent discrete sources of this particular fluid. Such inclusion could be analyzed to confirm they are ore bearing potentials. So, this is a typical synchrotron source X-ray florescence spectra. So, this method looks quite promising and it address to out to address outstanding issues of ore fluid and we expect to see more on this particular technique in the future.

(Refer Slide Time: 24:46)



Review:

- Microthermometry constitutes the backbone of fluid inclusion research and efforts should be on to make microthermometry more dependable and definitive (efforts are already on such as the HDAC)
- Data on microthermometry should be augmented by data generated from bulk destructive analysis and the data are proved to be quite meaningful on many instances – the instrumental methods such as Ion Chromatograph and ICP MS are easily accessible and straightforward.
- LRM stands as the most easily adoptable and accessible technique for in-situ non-destructive analysis (easier than FT IR) and there are ample scopes for making this technique more dependable (Cryo Raman)

So, these are some of the in the techniques which are currently in practice for analysis of inclusion. Essentially with an with an objective of augmenting the data that we generate by our micro thermometric experiments.

So, just a quick review that micro thermometry still backbone is still the technique which will give us the bulk of the data on fluid inclusions, and the most important data on the fluid inclusions, because, it as far as the thermal resigned is concerned, whether the ore fluid was a what kind of temperature range high, low. From that if we speculate whether the fluid could be metamorphic fluid, magnetic field contact fluid or material fluid and so on.

Here it would be worthwhile to make a mention about a recent development has so, already of course, more than about a one and half decayed and old or more. So, when we are experimenting or when we are doing them micro thermometric study and conventional heating freezing stages we are conducting the experiments in one atmospheric condition. That is reason why all these problems of decrepitation have inclusions and so on the problem we have not been able to overcome.

Now, then recently there has been a development of a particular kind of hot and hot stage which is basically the hydrothermal diamond and we will apparatus, this HDAC this hydrothermal diamond and we will apparatus has when a very significant development in a recent past in which it is possible to carry out contact micro thermometric experiments at precious more than one bar.

So, that even if they were depending on what kind of pressure which will be able to generate there. We will be able to succeed in getting the homogenization temperature of in most of the cases like the aqueous carbonic inclusions where, the inclusions decrypted because a building of a high internal pressure. And we expect to see a more wider use of this hydrothermal diamond and we will sell which is as called as a measure is a very significant improvement to the micro thermometric experiments.

And so micro thermometry still the most dependable and the now it gives us the first and information about the fluid characteristics. But then micro thermometric data should be augmented by data generated from bulk and destructive analysis like what we have given in the situation the in very simple analytical method like ion chromatography which is the instrument is very simple.

And the working principle and the handling of the equipment etcetera will always make it is a choiceable technique for any fluid inclusionist. And the only if we could somehow overcome the problem of the multiple generations of inclusions or keeping the mind keeping in mind the uncertainties that and that is kind of we are introducing.

And situations corresponding to lower temperature epithermal environment in which see this inclusions which are not subjected to much of a later recalibration or later disturbances. And ion chromatographic method could be very efficient technique to understand the or to further characterize the inclusion fluid in terms of their concentration of different titanic species.

And now we would also like to see because till so far we can so, only problem is that now, this kind of analysis we have direct we cannot get the entire range of cations analyzed by using one particular stationary phase which is present in there are column.

For example, if you want to analyze copper kind of base metal, different type of detector is required or which we want to go for the transition metals, different type of a column is required for the stationary phase. And but then, they could they are still within the they still could be achieved without much of problem in a in a laboratory to generate such kind of a bulk destructive analytical data like and what is possible in an ion chromatograph.

So, laser Raman micro spectrometry stands as the most easily adaptable and successful technique for in-situ non destructive analysis and it is very widely used. And we hope to see the further improvement on this particular technique and the including the cryo Raman which could also be practiced with for more commonly then what it is being done now.

So, with this we conclude our discussion on the one analysis of fluid inclusions covering techniques of bulk destructive in-situ destructive and in-situ non destructive techniques are they would there come up there come up phase to have to produce better quality of data better science while addressing the issues of the fluid, it is origin, it is role in processes that we are interested in.

Thank you.