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

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Lecture - 31

Analysis of Fluid Inclusion

Welcome to our discussion of the lecture series on Fluid Inclusion in Minerals. Over the past few weeks we had a quick to browse through the fluid inclusions that we encounter in different types of a environments and different types of processes that are resisted by fluid.

We browse through their characteristics; the methodology in brief is to how to look at them and within the time frame of this lecture series. We discussed about the data that we could acquire from the micro thermometric experiments of derives types of fluid inclusions that we have that we see in the host minerals which are also pretty drivers, well majority of them are actually done on course host in the there are a lot more on minerals from which fluid inclusions can be studied, when the samples are taken from the relevant samples, the relevant rock exposures when we study various environments and pertaining to various processes.

And we have had a brief ideas to how to apply the results of micro thermometric analysis to understanding of the processes in an ore forming environment, in metamorphism and how the fluid inclusions are deformed, recalibrated and how to overcome many of the problems that arise because of that and how to make causes and judicious, interpretations to our data that have acquired through micro thermometry.

Micro thermometry gives us the very fast and information about the fluid inclusion characteristics and intern the characteristics of the fluid; that is that was responsible of that give rise to the rocks that we are studying with a particular with the problem that we have in mind to address. Then it is mandatory, there is no substitute to micro thermometric analysis and the instrumentation involved also is not that very expensive and any fluid inclusion laboratory anywhere in the world can have such kind of fluid inclusion stage or even more of such stages are different types the one which we discussed could operate in a temperature range of 600 or 700 to minus 196 degree

Celsius. There also other in could other designs of this kind of micro thermometric apparatus where inclusions can be studied at much higher temperature.

And for example, as we saw and some of the over environment the fluid to temperature could be even higher than 600 degree Celsius. And we will have a limitation of using stages which will operate between even within that particular range 600 to minus 196.

So, there are fluid inclusion stages which are designed to operate at higher temperature; and also suitable for study of the melt inclusions so, which we have not covered in this particular lecture series. So now, we would so, any and we also have realized the limitations of micro thermometric experiments that results that is obtained from them, in terms of the chemistry of the fluid inclusions.

Although, we have a good idea about the thermal design about the thermal characteristics, as far as the precise chemical composition of the fluid inclusion that we see would still involve a bit of over simplification like expressing them in weight percent N a C l equivalent. And even in case of inclusion, which are reach in volatile species.

So, in this particular weak we will attempt to discuss some of the methodologies and the instrumentation and technique that are involved in analysis of this fluid inclusions. And any fluid inclusion micro thermometric data and that is generated on any kind of samples that we are studying. If it is supplemented by such kind of analytical data then, the quality of the data our, our understanding about the fluid is definitely enhanced. And we are in the position to a present a little better quality of science. Then what is possible with only micro thermometric data needless to mention that even most of the work that were being done in the earlier stages of development of this particular branch of study used to rely mostly on micro thermometric apparatus.

But still very primitive type of operators used be design like the crushing stage whose description will be available in some standard textbooks and old literature. Where the fluid inclusions if there is content in small fragment of the hosting host mineral can be crushed in particular in very specific type of liquid medium like oils, oil some medium of some specific gravity refractive index the samples could be crushed.

And the volatiles release from those samples could be studied entities have some ideas to what could the volatile could be. So, in this from this point onwards will be discussing about the analysis of fluid inclusions.

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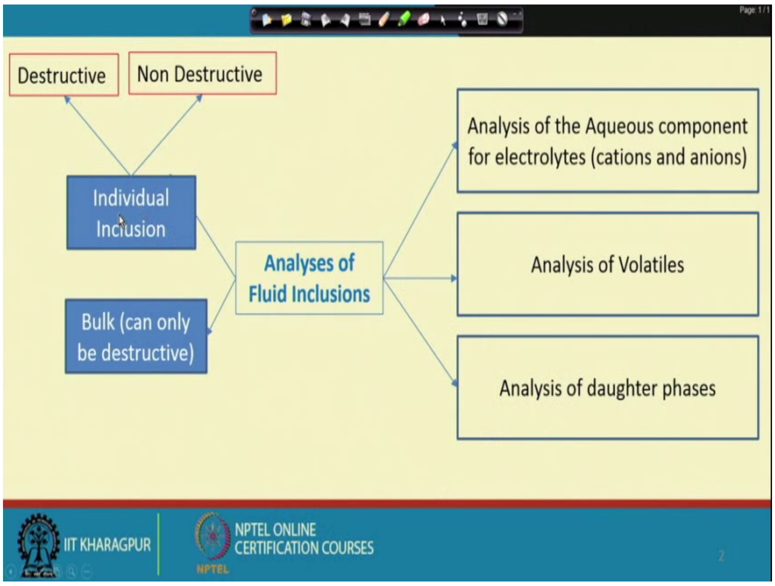

Destructive

Non Destructive

Individual Inclusion

Bulk (can only be destructive)

Analyses of Fluid Inclusions

Analysis of the Aqueous component for electrolytes (cations and anions)

Analysis of Volatiles

Analysis of daughter phases

So, if we look at or if you see we can either think of that we can analyze the sample in bulk and can have some idea about the characteristics of the fluid content in them, because from the various photographs of fluid inclusion that we have seen. So, far we could see that they are variably populated with fluid inclusions of different types.

And we can have some idea as to what could be the volume percent or mass percent of the fluid in any particular host that we are studying from while doing the routine petrography and examining the fluid inclusions in the minerals. And we have seen that there is a wide range of variations in them. So, keeping that in mind we can possibly to the analysis of fluid inclusions you can broadly categorizing to two that they could be either on individual inclusions or on the bulk.

So, bulk analysis will always be destructive because, when we take bulk sample. And we extract the fluid inclusion from them by any by either over heating them and that repetition or of polarizing them crushing them in some liquid medium to get a leachates. So, all it always has to be a destructive technique so, this bulk analysis and we can also go for analyzing the individual inclusion and those will be our micro analytical methodologies techniques using precise high and sophisticated equipment and those in those kind of analysis also we could have either non destructive or destructive.

So, nondestructive in the sense that they inclusion will not be destroyed and can be further studied or can be preserved for any further, type of analysis of to be destructive that we destroy the inclusion take out the content from the inclusion cavity and do the analysis. And as far as the fluid inclusions are concerned about the content of the fluid inclusions, we can think of in these three different broad components of them that either we are basically; you would be attempting to estimate the concentrations of various electrolytes species, various aqueous pieces in the liquid, in the aqueous component, the liquid water component of it. The various cations and anions or we could analyze a non aqueous part what we are seeing is volatile also could be saying the analysis of the non aqueous component like; carbon dioxide, methane, nitrogen H2S argon and so on.

What we have seen that inclusions can fluid inclusions can have an appreciable concentrations depending on the kind of geological environment in which the process is operating. And the analysis of the solid mineral phases which have there in the cavity of the mineral, and in most of the cases their a precipitate out of the inclusion fluid with changing pressure temperature condition, when the particular mineral attains saturation or at times a could be accidentally captured solid phases.

So, this will be the general idea would what we understand about the fluid inclusion analysis.

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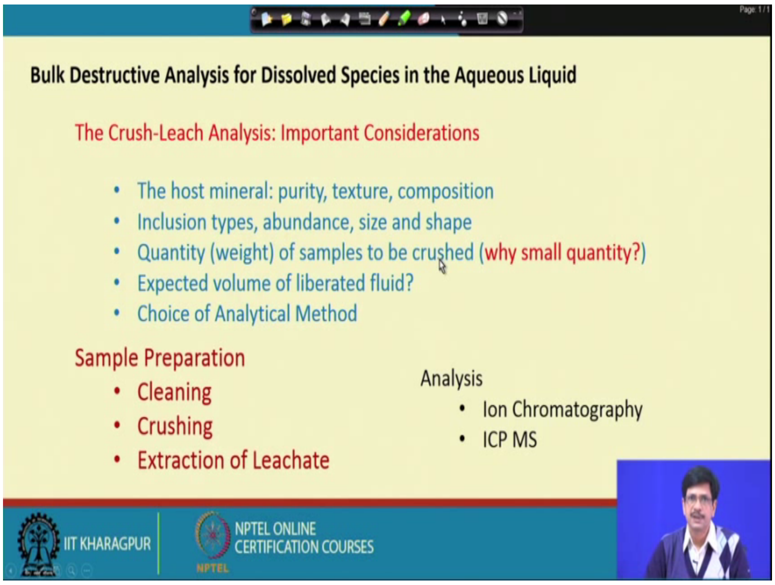

Bulk Destructive Analysis for Dissolved Species in the Aqueous Liquid

The Crush-Leach Analysis: Important Considerations

- The host mineral: purity, texture, composition
- Inclusion types, abundance, size and shape
- Quantity (weight) of samples to be crushed (why small quantity?)
- Expected volume of liberated fluid?
- Choice of Analytical Method

Sample Preparation

- Cleaning
- Crushing
- Extraction of Leachate

Analysis

- Ion Chromatography
- ICP MS

So, the bulk destructs over with will start with. So, before this before getting into any of the details it is to be kept in mind that this analysis of the fluid inclusion is the responsibility of the fluid inclusionist himself or herself. And the unless it involves very high and in very high and high sensitive high and equipment like; secondary and mass spectrometer like a scenes or a synchrotron radiation x ray fluorescence, spectrometry those which will always be operated by experts and sometimes the analysis.

So, the fluid inclusion is did not have to or may not be possible on the part of the person to be getting a full details on the principles of the analysis of this with this kind of high and equipment. And it those situations will only be interested in getting the result in terms of what we actually wanted. But there are certain instrumental method certain analytical procedures methods, which has to be carried out by the fluid inclusionist himself.

Because, it is the background study which plays a major role in producing the quality of the data the nature of the data and the quality of the data will be very much dependent on the care that is been taken. And some of these equipment which we can call is the small end equipment like and ion chromatograph or a even sometimes Raman spectrometer which will be discussing in detail. Those instrumental details the little bit of the working principles it is always better to have some idea about them and those will be discussing to sum greater degree of details.

So, if we start with the bulk destructive analysis for dissolved species in the aqueous liquid here, we are limited by only releasing the aqueous liquid part and analyzing it for the dissolved anions on the cations. Some such procedure which is followed for a very good time for a long time, now, is a crush leach analysis.

Essentially, it means that we take some take a particular weight of sample and we crush them in a the annoyed to water double these two water with pure purified water, ultra pure water which is free of any such dissolves species that were interested to analyze. And then, release the content of the fluid into that medium of the medium of and pure water.

And then take the content and analyze and some suitable instrumental methods. Now in such some such kind of crush leach analysis even though it is in practice where for a long time there are certain limitations. First of all the things that we have to keep in a mind that the host mineral in which we want to study or analyze the leachate, what you will get in this crush leach analysis? In essentially, a volume of the liquid which is called them as a leachate which will be our analyze in which we very interested to analyze the concentrations of different aqueous species.

So, the purity of the host mineral for example: if we want to analyze this element this ionic species like sodium, potassium, calcium, magnesium, ion and the anion species like; chloride, fluoride, and the bi carbonate and carbonate and so on. Then, it is always essential to see which host mineral in which we are going to do the study carry out the study.

They should have a very limited solubility under the room temperature condition when we are crushing them and the they are minerals water, if their themselves will contaminate the solution. Then, the analysis will not be dependable provided would be we work out to a great degree of details as to what will be the solubility of that particular host mineral.

And then depending on the room temperature solubility what concentration of any of the ions that it is going to contribute, but to the best possible practices; whenever, we doing it in host mineral, we have to ensure purity of the host mineral; that means, if we are going to crush the extra to leachate from inclusions hosted in faults.

Then, we have to see to it that the samples that were taking it is pure, study it textural relationship if there are any other mineral that is associated with heat like proteus culture, Russum clay or some other file sutical So, file sutical mineral associated with them or any other alteration mineral and how to actually purified a simple how to get a pure fraction of the host mineral that we want.

Another important crucial aspect to the inclusion types, their abundance, size and shape. Because, if we see the inclusions there so, much of mixed type of aqueous and aqueous carbon a inclusion that we know that what exactly we expect here their abundance and size and shape will be a governing parameter. Because are there is a variation which we see in when it across different sample that we take from different environment.

Size and shape play important role because, we are going to crush the sample in order to release the fluid content in the inclusion. Then the quantity of the samples actually how much we should crush because, here before we had precise analytical equipment available these there in which very small quantity a very small volume of the analyte suffice for them for the analytical work.

But, before that to get because if we say that in an ideal situation if the host mineral like quartz, if I doing some kind of a modal analysis we know that so, this 0.1 percent and volume of the mineral is the fluid. And then, if we want to extract a few CC's few CC's of this leachate and how much of solid we must crush.

So, these this will be availability of high precision are equipment like say for example, and ion chromatograph in which we can analyze with very small volume of fluid the liquid as small is about 20 micro liter or so. Then, we actually need very small volume of the leachate and in that case we can also referred to crush a small weight of the samples and because, to in order to extract a larger volume of their leachate to crush the host mineral.

Since, we still have to adopt where to have a get prototype crushing of their polarization of the samples because, we cannot do it in any other polarizer because in that case you would not be knowing exactly what kind of contamination will be introducing. So, it is always easy they become shape and should be method becomes more adaptable.

If a small weight is for example, a fraction of 5 5 to 10 grams of the host ore, I would be sufficient to release the fluid that will be calculating and then, the leachate that will be preparing just about within in a 10 10 to 15 CC of the purified water in which will be doing the crushing. Then will be enough for analyzing other the leachate using some very high precision equipment like a ion chromatograph or a ICP MS.

So, we should have some idea about the expected volume of the liberated fluid, which will be variable and it will always be advisable if such kind of work would be done for example, doing some modal analysis may computed assisted the modal analysis like an anyways analyzing. So, the software in a program, if we could have such frames in which we can calculate the area percentage of the inclusions and then can integrate to have some idea about the what is the volume percent of the fluid in the particular host we are studying.

Then, we can have a better control because, will be analyzing in our leachate and then we have to back calculate in terms of how much of to the actually fluid which are actually volume of the fluid that likely to have been extracted. And you will have to multiply that that factor to convert them to the composition of the inclusion fluid. And the major problem in this kind of an exercise is that when we are crushing a the bulk of the sample in the sample we know that there can possibly be more than one generations are fluid inclusion future entrapped.

So, this place a very careful study to actually acceptance as to how many because, we will not be possibly be able to circumvent the problem fully. But, we can always see that fought in the different generations of the secondary inclusion which are in the heel cracks have some idea about them.

In some of the cases, it can always be that if the heat particular sample to a certain temperature in which we know that the secondary inclusions if they happened to be of too much lower temperature and much later entrapment in the host mineral. Then, it would possibly be is a it may be possible to get the secondary fluid liberated before we really go for the crushing of this particular samples.

And we initially we are reducing the sample size to a refute millimeters. So, that we can kept keep it in a we can crush then in a agate motor and of procedure and by that time also how we the possibly released good amount of the secondary inclusions.

But, then they will still be there and our results of analysis will always involve that degree of uncertainty which will arise from presence of inclusions of many different generations. So, the sample preparation would involve a elaborate and thorough cleaning and in this process of cleaning it will always be easy will be always be advisable to go for cleaning or at higher temperature in using ultra pure water.

And then maybe because here if we you want be I will to use kind of exceeds to clean the samples because, they will contaminate the analysis. For example, if we use nitric acid to clean our samples, then the nitrate concentration in our few in our leachate may not be very dependable. And then it also, and so it would be advisable to go for rather kind of electrolytic cleaning to remove any other kind of adsorbed ions are any other elemental species that are there on the inclusion on the solid surface of the mineral.

So, we need to do elaborate cleaning before we can actually take the samples for extraction of the leachate. So, the crushing has to be done by in a again and agate motor and within the within a the purified water medium and we will reduce it, reduce the size to what is attainable in agate motor almost like a minus 200 base which will be roughly about 75 macrons size.

So, that also gives us an idea that if we reduce the samples to size of minus 200 mesh what is the possibility of what would be the percentage of the inclusion that really I likely to have an opened and what volume of the inclusion fluid we would be expecting. And then, we use the liquid medium in such a way that make it make it up to a volume of known volume of the 10 or 15 CC.

In most of the cases we use 10 CC volume of the leachate and then now we decide that which method of analysis to you going to do? Because, ion chromatography will give the concentrations in the inform of the ions and the more precise analytical equipment like and ICP MS will give the elemental concentration.

So, it depends on the availability, but it is always a advisable that we can do an ion chromatography analysis and if the possible combine the data within ICP because, ion chromatography will have a limitation. In the ranges of the elements of the ionic species that could be analyzed although we know that in our sample in our inclusion fluids the major cations will be the sodium, potassium, calcium, magnesium, ion and others will be in place quantity.

And sometimes we were also if we are more interested in our your studying essentially an ore farming environment then it is will be interested in estimating the base metals the transition metals like; iron, cobalt, nickel, copper manganese. And in fact, these are the areas which lots of work lots of research goes on and this kind of instrumental analytical techniques are constantly being upgraded.

So, that they become more and more versatile and there is provision for analysis of more and more of this ion is pieces. But ICP MS would definitely have a far more range of the elemental species to be analyzed then in an ion chromatograph.

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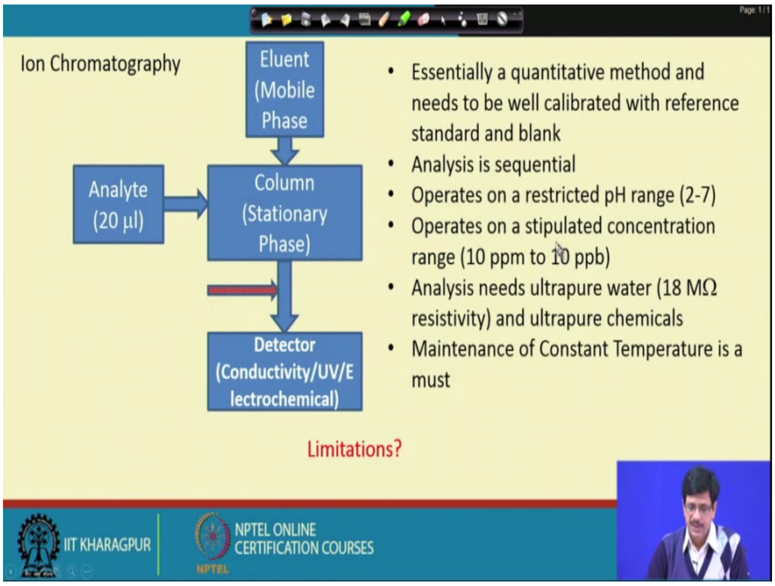

Ion Chromatography

Eluent (Mobile Phase

Analyte (20 μl)

Column (Stationary Phase)

Detector (Conductivity/UV/E lectrochemical)

- Essentially a quantitative method and needs to be well calibrated with reference standard and blank
- Analysis is sequential
- Operates on a restricted pH range (2-7)
- Operates on a stipulated concentration range (10 ppm to 10 ppb)
- Analysis needs ultrapure water (18 MΩ resistivity) and ultrapure chemicals
- Maintenance of Constant Temperature is a must

Limitations?

So, I will just discuss a little bit about the principles of operation of ion chromatograph. So, ion chromatography is essentially what we understand is an exchange ion exchange chromatography.

So, we can very very simple way and this within the limitation of this particular lecture series. We can explain that how it works we want to have our analyte in a volume of 20 micro liter minimum or it can be sometimes you may need to little more but a 20 micro liter quantity could be enough.

And that is injected to something which essentially we column which contains a phase which is a stationary phase which is like a like some material which have come out through research. And the properties of property of this particular stationary phase is that is not when the analyte is injected, the ions all the ions in the in the solution they will get attached or will be absorbed or will be attached to this particular material which is there in the column, which is could be ragin or some kind of material which is has the property do that and the method works in the principle of release of those ionic species with their attached to the mobile phase to be to be released at our order to have variable retention time. So, that if we make a mobile phase with to eluent the particular ionic ions from the column.

So, there will be released at different for a different they will have different retention time. So, there will be released very efficiently subsequently one after the other, little bit depending on their charge and their surface characteristics and many of the chemistry which is which cannot going to details very much.

So, it is now this analysis as we know it is quantitative analysis. So, it will be working on standard based reference standard with known concentration, this kind of standard known concentration standard solutions can be prepared in the laboratory. And which you retained which is (Refer Time: 26:17) for many of the cations and there are multi anion standard which are available commercially or also can be prepared in the laboratory provided you provided one ensures very very pure chemicals and also a very clean environment in the laboratory.

So, it is essentially the quantitative method and needs to be well calibrated so, it also works on the concentration ranges of the calibration standard actual is showing a little bit now. So, this analysis is sequential the ions are analyzed one after the other for examples in case of a, and of an anion will have fluoride chloride bromide nitrate phosphate, sulphate to be analyzed sequentially. And it operates on a restricted p H range of the analyte range 2-7 is operated on stipulated concentration range from 10 ppm to 10 ppb, where the beauty of this equipment of the efficiency of the equipment lies in the fact, that we can prepare a linear calibration line in this range of several orders of magnitude variation in the range of concentration.

And the analysis needs ultra pure water almost like 18 mega ohm resistivity water and alter pure chemicals. And this entire procedure works because when we see here that this analyte is injected to the column and the column is being constantly flashed by the mobile phase, the mobile phase in different types of analysis like anions and cations are well specified depending on the chemical principles.

For example, for a typical analysis will be a preparing a very low concentration of bicarbonate and carbonate which will eluent the anionic species like; fluoride, chloride, bromide, nitrate, phosphate and sulphate at different point of time. And the detected by various types of detectors there could be and most of the cases that detected by a conductivity detector. Which will one give the response and in terms of the concentration of the particular ion and they got the conductivity and that is the conductivity difference that is resulted because of the release of this particular ion.

And when a conductivity is actually working on them having the electrode where the anions and cations are getting deposited and the potential difference is created and it is work on them particular principle. One can also have a UVE visible type of detector for which is specifically use for the basement like transition metals where, there more on the on their observance and there absorption characteristics of this kind of elements of the or there could be electrochemical detectors.

Similarly, there are various so various types of various designs for various materials which are used as columns in analysis of different groups of anions. For example, cyanide will be requiring a different type of a mobile phase sorry, the different type of a column. And so, the limitation is that they analysis in any case will be incomplete because, it is not possible to analyze all the as a enough now. So, the limitations are actually getting overcome gradually and one would hope that this kind of instrumental methods will actually give very precise and very complete analysis.

Because, as we know that in any particular ion ionic analysis if you major the anions and the cations ideally, the summation of the charges of the anions and the sum of the charges of the cations would balance and within the permissible limit. And if you just major a few anions like fluoride, chloride, bromide, nitrate, phosphate and sulphate and some cations like; lithium, ammonium, sodium, potassium, magnesium, calcium definitely there will be good amount of charge imbalance.

But, this have very important purpose of characterizing the fluid in terms of the not only the ionic species, but their ratios there. So, that we see the special variation in the ratios of the different elements species and can draw important inferences on the fluid inclusion.

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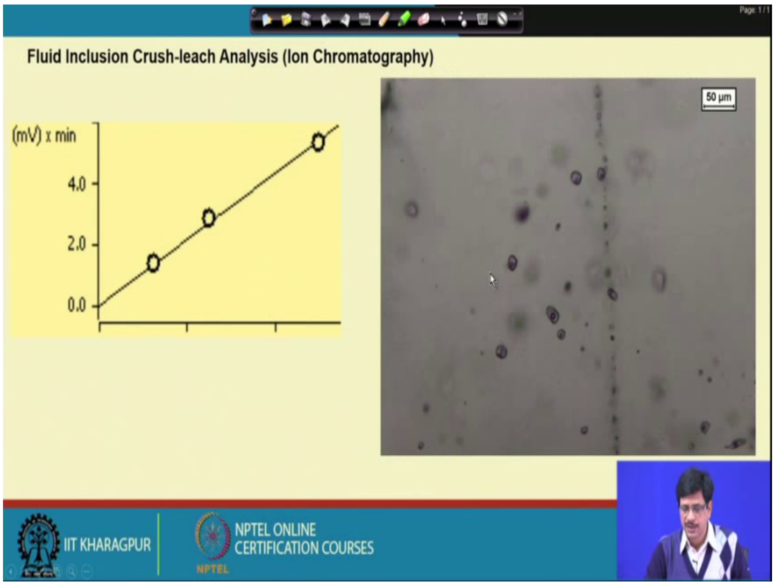

Fluid Inclusion Crush-leach Analysis (Ion Chromatography)

So, here is an example that have taken from a sample taken from Malanjkhand copper deposit where we could see the fluid inclusion aqueous biphase inclusion and we could see that there are primary in biphase inclusion and also there are trails of secondary inclusions. And so, we know that what kind of so; if we could somehow get rid of the inclusions from the secondary trails, then it will power inclusions analysis will be more reliable.

But, we have to anion we have to interpret the results within that frame work, it is showing just an example is to how an ion chromatography analysis, this is calibration and this calibration can be checked with its root mean square error and are reproducibility and the statistics.

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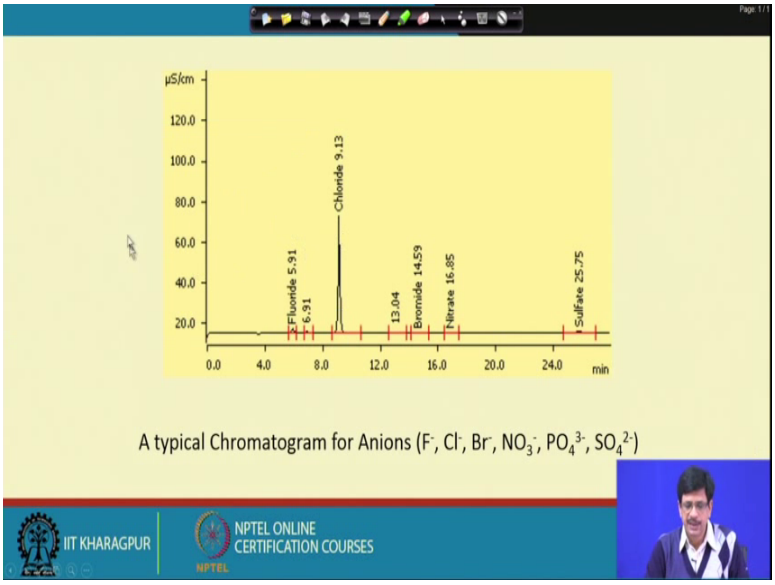

A typical Chromatogram for Anions (F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-})

And here is an typical example of a chromatogram for the different using one particular column in which the six anions could be analyzed here we do not get any phosphate because, the fluid that we extract that we leachate that are extracted possibly did not have a measurable concentration of phosphate. Because every recruitment has the concentration range and below which we say that it is below the detection limit and we cannot analyze it.

So, we could see that this is how the peaks they there occur on a chromatogram which is which is the x axis is the time in minutes starting from 0 and you could see that it almost takes about 27 and 28 minutes for a leachate to be analyzed for it is anion concentration, on the y axis is the conductivity in terms of microsiemens per centimeter. And we could see that a very nice and the very straight baseline and we see the peaks here and the where we have our reference standards in which the concentration are known in ppm to ppb ranges.

Then, from that by taking the area covered under the curve which is also done for the standards the concentrations absolute concentration of these anionic species is calculated from this kind of chromatogram.

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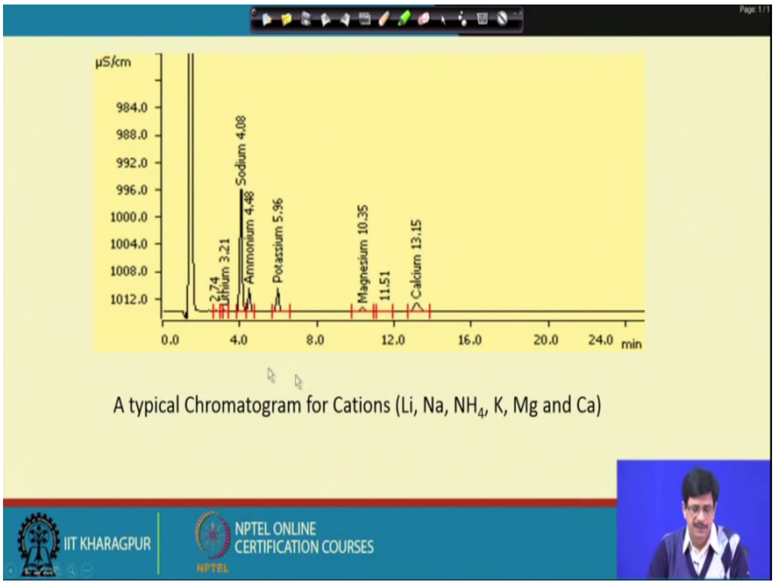

A typical Chromatogram for Cations (Li, Na, NH_4, K, Mg and Ca)

And this is an example of a analysis of cations, lithium, sodium, ammonium, potassium, magnesium and calcium. So, these are the analysis which is done by again similarly the same conductivity detector by the conductivity plotted on the y axis and the time is on the x. Axis and you could see similar kind of duration of time is required for and it is always advisable to have such kind of peaks well separated.

So, that the peak area could be accurately measured, sometimes if the mobile phased element concentration is increased then we can always get this get this peaks so, get the total time of analysis reduced. But, there should be a tradeoff between what could be the how much of time that is to be afforded for this analysis for persess p, dependability of the accuracy, and it is always advisable to have the prescribed the concentration of the mobile phase. So, that we could get very well workable out the peaks of this kind of the ionic species for their dependable analysis.

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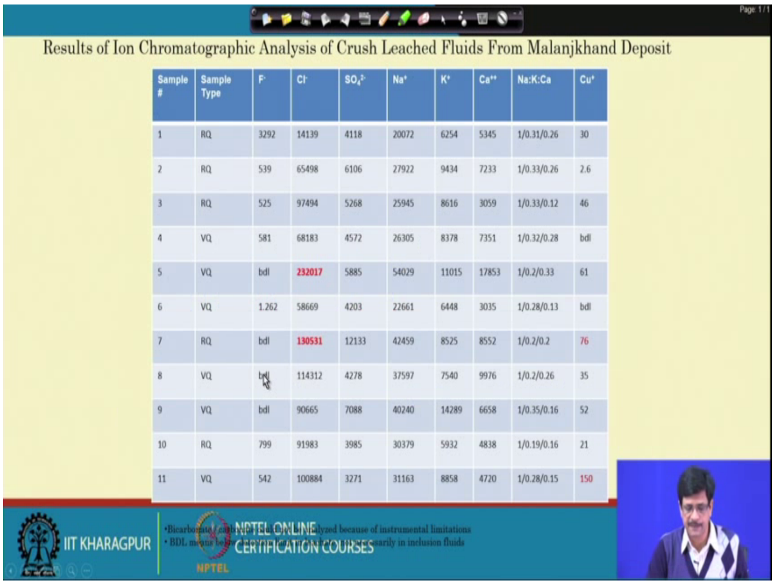

Results of Ion Chromatographic Analysis of Crush Leached Fluids From Malanjkhand Deposit

Sample #	Sample Type	F^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{++}	Na:K:Ca	Cu^+
1	RQ	3292	14139	4118	20072	6254	5345	1/0.31/0.26	30
2	RQ	539	65498	6106	27922	9434	7233	1/0.33/0.26	2.6
3	RQ	525	97494	5268	25945	8616	3059	1/0.33/0.12	46
4	VQ	581	68183	4572	26305	8378	7351	1/0.32/0.28	bdl
5	VQ	bdl	232017	5885	54029	11015	17853	1/0.2/0.33	61
6	VQ	1.262	58669	4203	22661	6448	3035	1/0.28/0.13	bdl
7	RQ	bdl	130531	12133	42459	8525	8552	1/0.2/0.2	76
8	VQ	bdl	114312	4278	37597	7540	9976	1/0.2/0.26	35
9	VQ	bdl	90665	7088	40240	14289	6658	1/0.35/0.16	52
10	RQ	799	91983	3985	30379	5932	4838	1/0.19/0.16	21
11	VQ	542	100884	3271	31163	8858	4720	1/0.28/0.15	150

- Bicarbonate/ [illegible] analyzed because of instrumental limitations
- BDL means [illegible] necessarily in inclusion fluids

So, these is an example that of the analysis that analysis that we got from the crush leach fluid from Malanjkhand deposit. This we could see that as expected amongst the cations the sodium is the most dominant one and amongst anion is the chloride which is most dominant one is going to almost like 23 percent say 1 percent 6 percent 9 percent 23 percent which as shown on red.

And the sodium percent, sodium also is the highest with presence of potassium and calcium which we could correlate from the observation of fluid inclusion freezing studies and the also the concentration of copper. So this, help us in making important interpretation in terms of the fluid chemistry and it is variation in space. And you could see here that the different ore types from the deposit which is labelled as RQ for we cause and VQ for the range. We could also make a very come good comparison between the fluid characteristics of from the different design you can drawing important conclusions.

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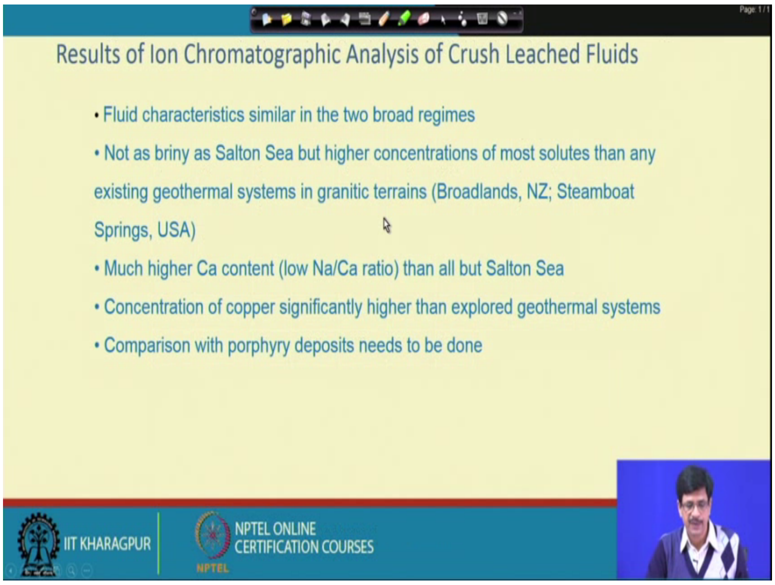

Results of Ion Chromatographic Analysis of Crush Leached Fluids

- Fluid characteristics similar in the two broad regimes
- Not as briny as Salton Sea but higher concentrations of most solutes than any existing geothermal systems in granitic terrains (Broadlands, NZ; Steamboat Springs, USA)
- Much higher Ca content (low Na/Ca ratio) than all but Salton Sea
- Concentration of copper significantly higher than explored geothermal systems
- Comparison with porphyry deposits needs to be done

And moreover, we could also make comparisons to some situations which we would like to compare: for example, thinking that it could represent a geothermal system, we could compare the fluid composition with as to with some known geothermal field fields like; the Broadland geothermal system in New Zealand or Steamboat or the Salton sea.

So, what we could see that ok, the higher calcium content is follow Na by Ca content in all this samples all the geothermal field, but Salton sea, Salton sea is possible a little more briny than what we see in the Malanjkhand situation. And this is just an example is to how we can use the ion chromatographic data and understandable there could you many more many more queries and curiosities questions will be there, but it is always better to refer to some standard materials for understanding, better understanding of the analytical protocols and procedures for enthusiast and people who want to and exercise it practice it on regular basis.

So, we will continue our discussion in the next class on the analysis of fluid inclusions.

Thank you.