

# **CHEMICAL ANALYSIS OF MINERALS**

**Quantitative methodology in mineralogy and mineral physics**

# CHEMICAL ANALYSIS OF MINERALS

- There are many different types of both qualitative and quantitative analysis available to mineralogists and petrologists. Specific techniques are chosen based on the goals of the researcher and the characteristics of the samples being studied.

- The four most important things to know before beginning any type of chemical analysis are:

- 1) What are the specific elements that we are hoping or expecting to analyze?

- 2) What are the characteristics of these elements (i.e. atomic weight and atomic number)?

- 3) What are the concentrations of the elements that we are dealing with (weight %, ppt, ppm, ppb)?

- 4) With which minerals or mineral phases are particular elements associated? This is especially important for in-situ analysis where knowledge of the phase is a first order control on the set-up of the analytical approach.

# OVERVIEW OF THE TYPES OF CHEMICAL ANALYSIS

- Broadly, we can divide chemical analysis into a few categories:
  - 1) Wet Chemical Analysis
  - 2) Powder or wet spectroscopy
  - 3) In-situ spectroscopy
- Once again, depending on your goals, some methods of chemical analysis may be more appropriate than others; however, there is considerable overlap between all techniques.
- In general, wet chemistry involves dissolving a mineral in an acid then analyzing the solution.
- Despite the variety of spectroscopic techniques, all involve some energy source that is used to bombard a samples in order to produce an electromagnetic signal that can be detected and analyzed.

# WET CHEMISTRY

- There are three basic types of wet chemistry; however, aspects of wet chemistry are utilized in the sample preparation for a number of spectroscopic techniques.

- 1) Gravimetric

- 2) Volumetric

- 3) Colorimetric

- For the most part all of these techniques require mineral samples that are relatively “pure”. These must then be powdered then dissolved once or over several steps.

- Mineral samples that are “pure” are often difficult to find in nature which may be problematic for these types of analysis.

## SPECTROSCOPIC TECHNIQUES

- There are multiple types of spectroscopic techniques that can be used to study the characteristics of elements that compose minerals.
- For the most part, all spectroscopic techniques take advantage of the same energy principals:
  - 1) By bombarding a sample with energy, electrons and/or neutrons can be excited.
  - 2) Electrons (and neutrons) can be made to change energy levels. Subsequently, they will relax back to their ground state and release characteristic energy
  - 3) Detectors can be set-up to look for specific characteristics of the electro-magnetic spectrum:
    - a) specific energies
    - b) specific wavelengths
    - c) specific frequencies

## SPECTROSCOPIC TECHNIQUES: ICP & AAS

- Both of these techniques take the sample preparation techniques of wet chemistry with some sort of reactive flux added as well.
- Dissolved samples are then sprayed into a chamber and heated to temperatures between  $\sim 1500^{\circ}\text{C}$  and  $\sim 6600^{\circ}\text{C}$ .
- Atomic absorption analysis (AAS) then uses a controlled flame and monochromator linked to a detector to search for wavelengths of light that are absorbed by the flame.
- Inductively coupled plasma (ICP) spectrometry uses a gas (typically Argon) to move the sample vapor into a chamber under high vacuum where both the sample and gas are heated such that elements will give off a characteristic wavelength of light.
- Both of these techniques require comparison to a set of known standards.



Laser ablation unit



inductively coupled plasma  
mass spectrometer

## SPECTROSCOPIC TECHNIQUES: XRF & XRD

- **X-ray Fluorescence (XRF)** is a technique that has broad application to mineralogy and petrology as multiple elements/ oxides can be analyzed for simultaneously.

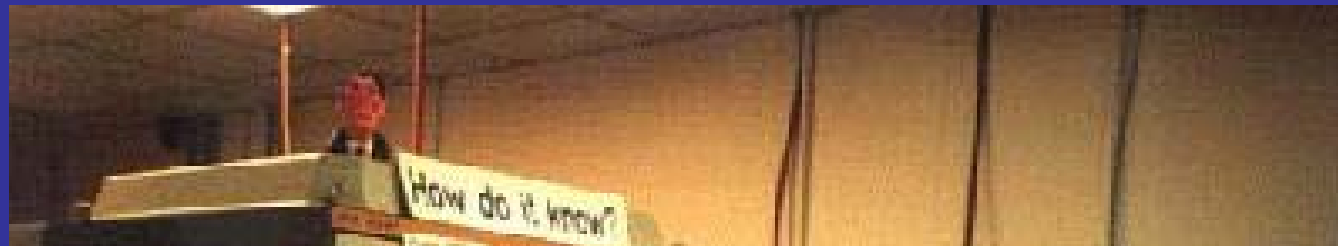
- 1) High voltage accelerates electrons toward a metal target to produce a specific fixed wavelength x-ray beam that hits the sample

- 2) Inner shell electrons in the sample are ejected and photons are emitted as outer shell electrons drop to inner orbitals.

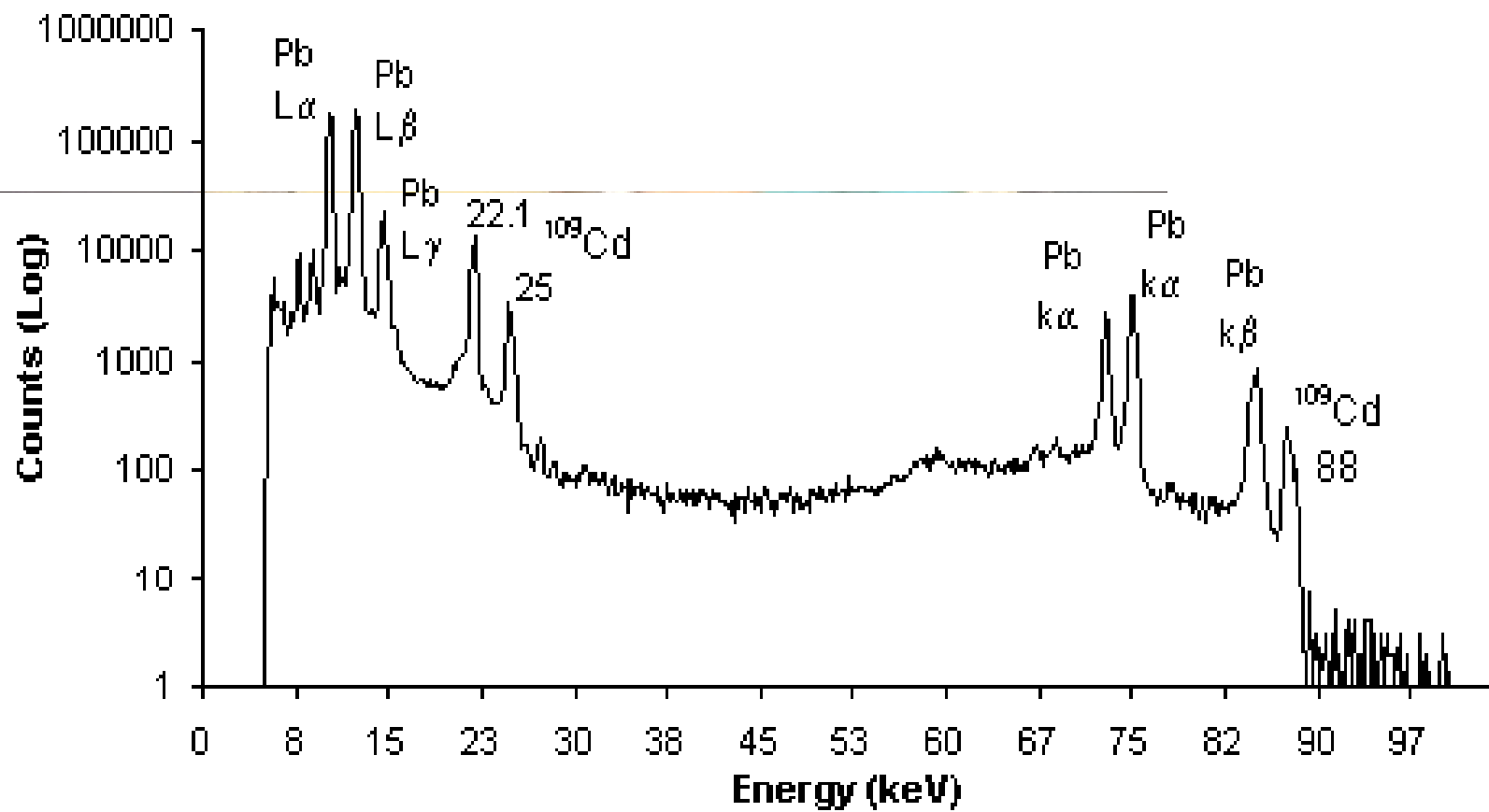
- 3) Photons have characteristic energies and elemental concentrations can be calculated with this technique by comparing sample intensities to a know standard.

- **XRF can analyze most elements heavier than oxygen (though there can be some complicating factors) down to the ppm level.**





### X-Ray Fluorescence of Lead from $^{109}\text{Cd}$



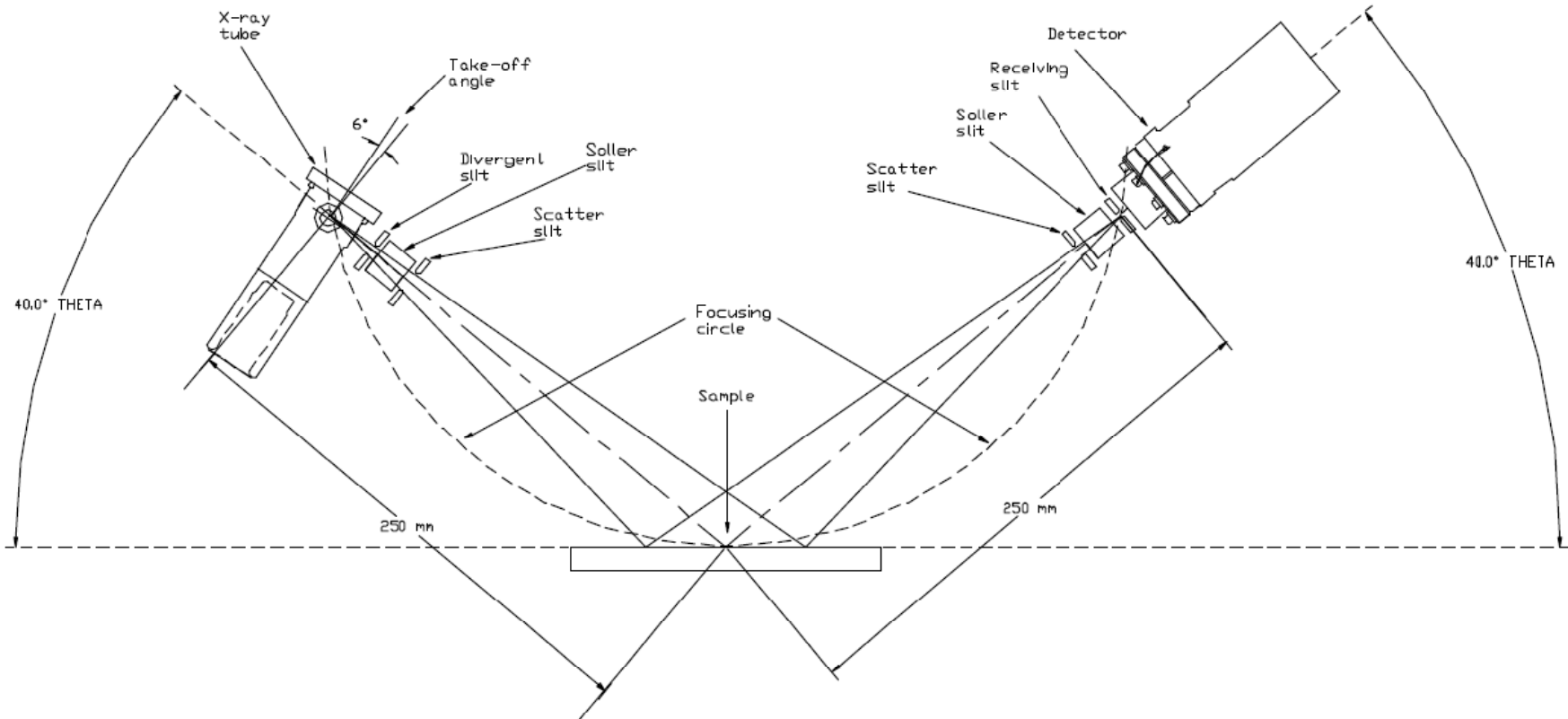
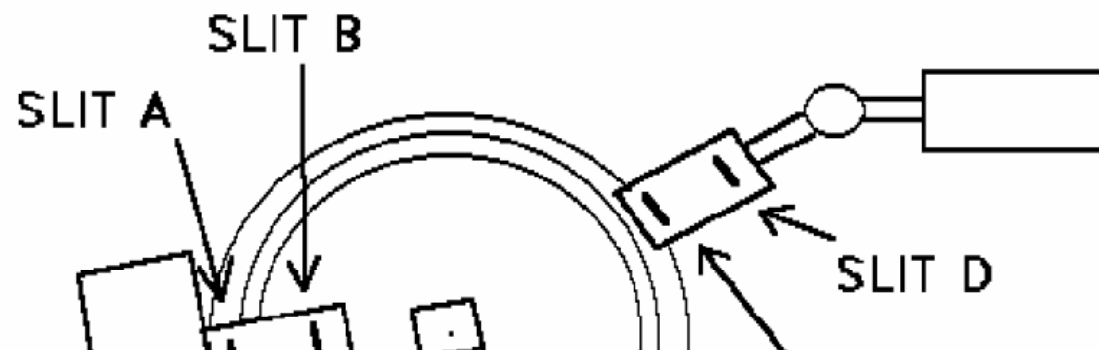
## SPECTROSCOPIC TECHNIQUES: XRF & XRD

● X-ray Diffractometry (XRD) is a technique that is really only appropriately applied to pure amorphous or crystalline substances and allows the user to learn a great deal about the structure of the compound.

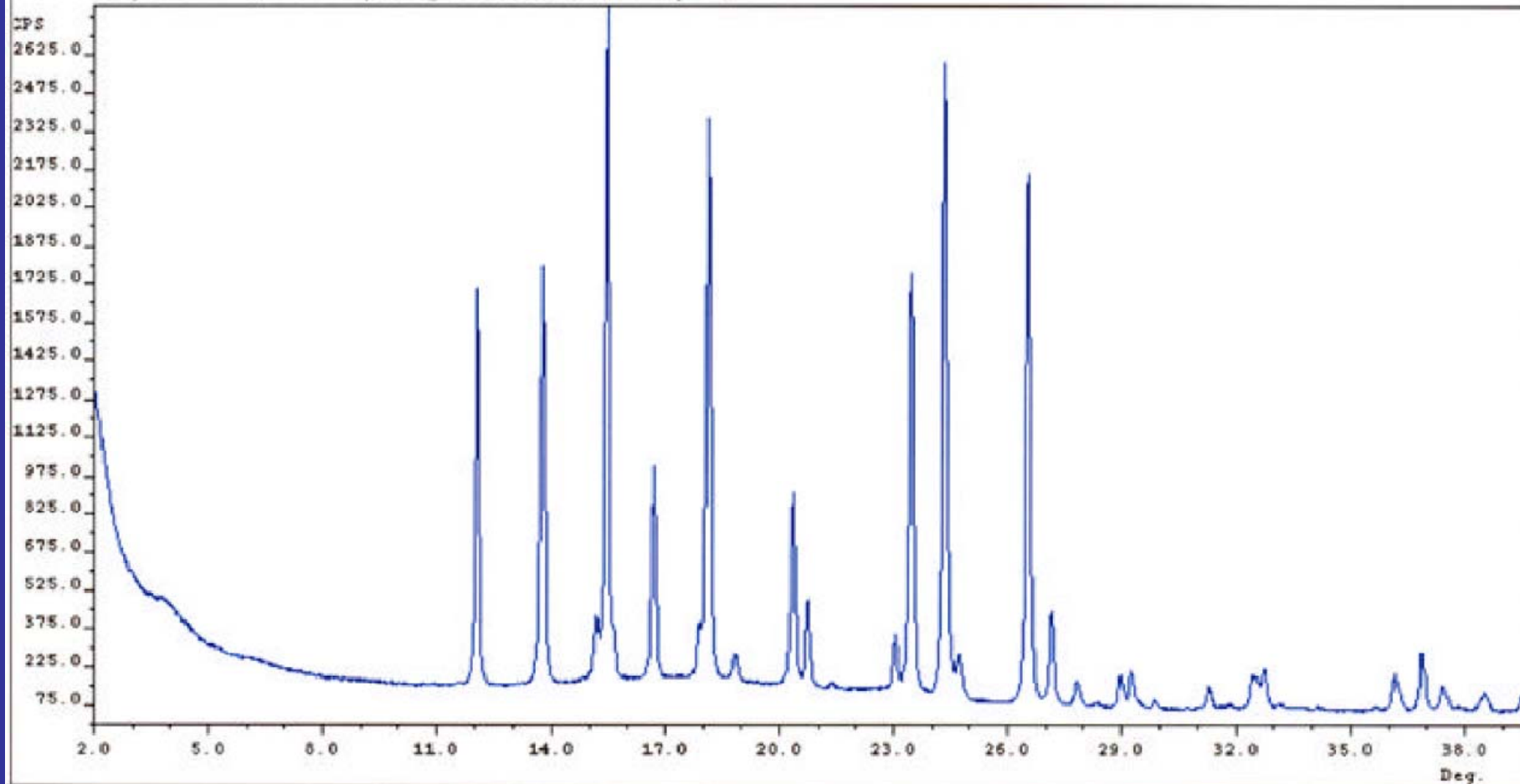
1) An x-ray beam is fired at a sample over a series of angles but keeping the source and target (sample) always at the same distance (called a goniometer).

2) The reflected or diffracted x-rays provide a 2-theta angle such that *Bragg's Law* ( $n\lambda = 2d \sin \Phi$ ) can be solved and we can use the d-spacing value to define the h, k, and l indices of the unit cell.

3) Using the three indices, we can calculate the dimensions of the units cell



File: TYLENOL, ID: ACETAMINOPHEN OVERNIGHT  
Date: 02/23/95 17:32 Step : 0.020° Cnt Time: 25.000 Sec.  
Range: 2.00 - 40.00 (Deg) Step Scan Rate : 0.00 Deg/min.



# SPECTROSCOPIC TECHNIQUES: EPMA & SEM

- **Electron probe micro-analysis (EPMA) basics**

- 1) A beam of electrons is generated and sent from the electron gun through a series of lenses and apertures toward the target (specimen).

- 2) The diameter and strength of the beam can be modified based on the current and accelerating voltage used to generate the beam.

- 3) Electrons in the specimen are excited and then, as electrons relax and fall back from an excited to a ground state they will fluoresce and generate x-rays

- 4) X-rays generated from the beam-specimen interaction are characterized by energy and wavelength to identify the element, intensity is used to analyze concentration

- A) Energy Dispersive Spectrometers (EDS): count number and energy of emitted x-ray photons

- B) Wavelength Dispersive Spectrometers (WDS): use specifically tuned crystals to pick-up particular wavelengths

Electron gun

Cathode

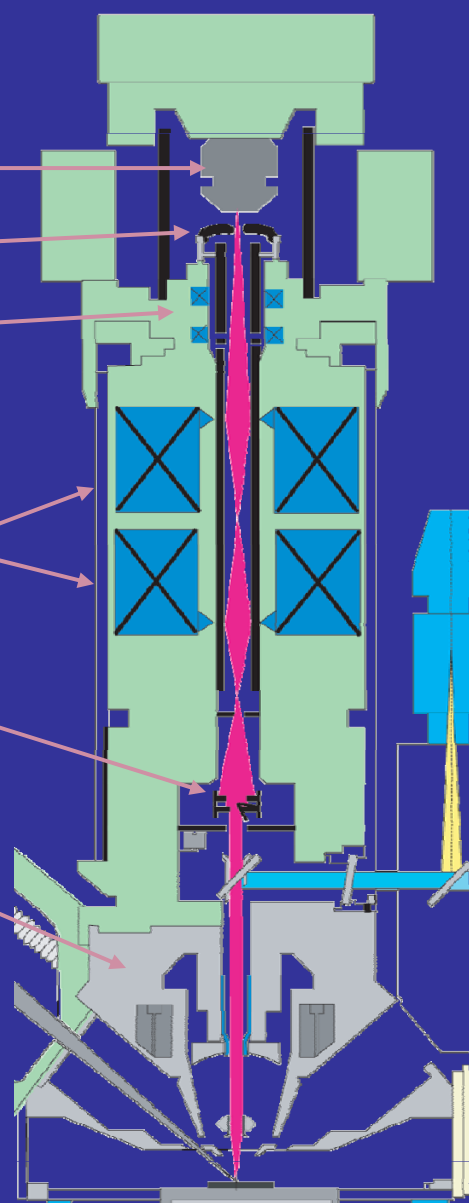
Anode

Alignment coils

Lenses  
condensers

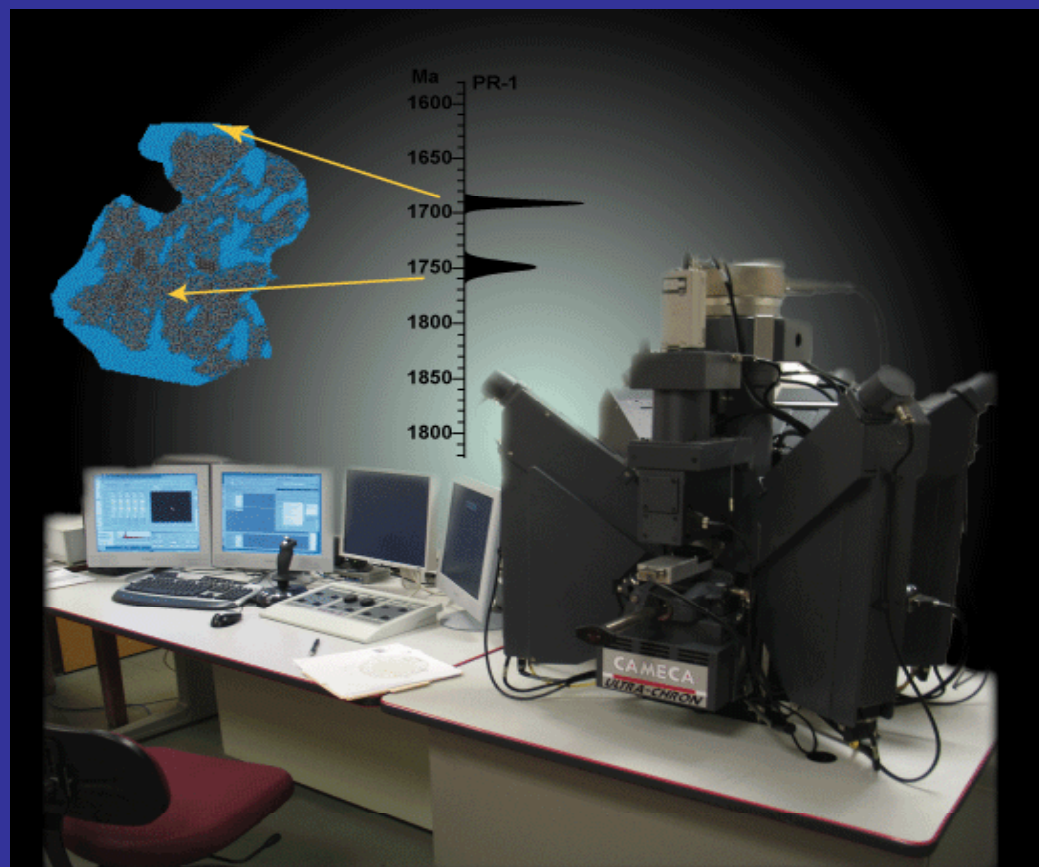
Objective  
aperture  
assembly

objective



sample

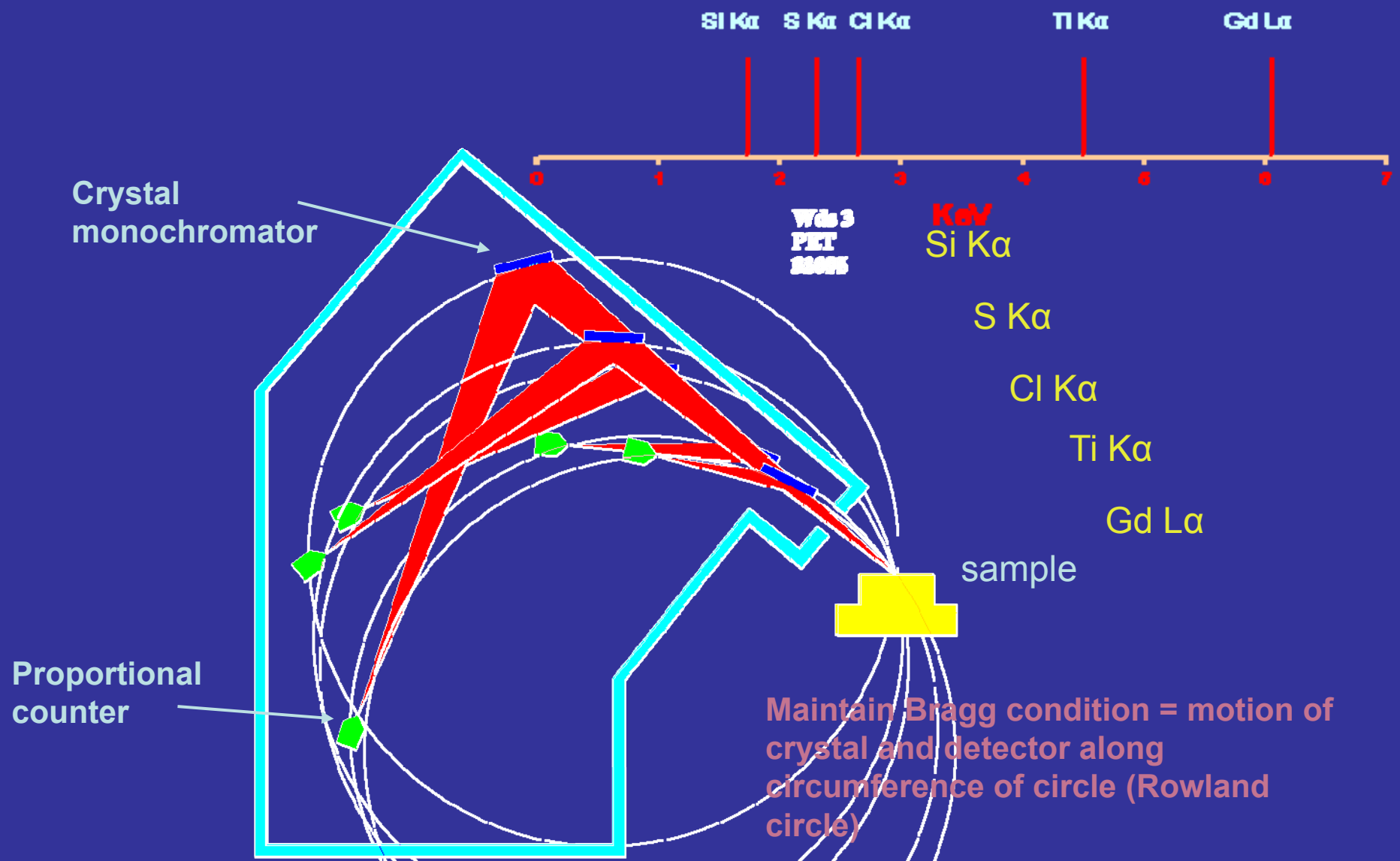
M. Jercinovic, 2007



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$d$  is known - solve for  $\lambda$  by changing  $\theta$

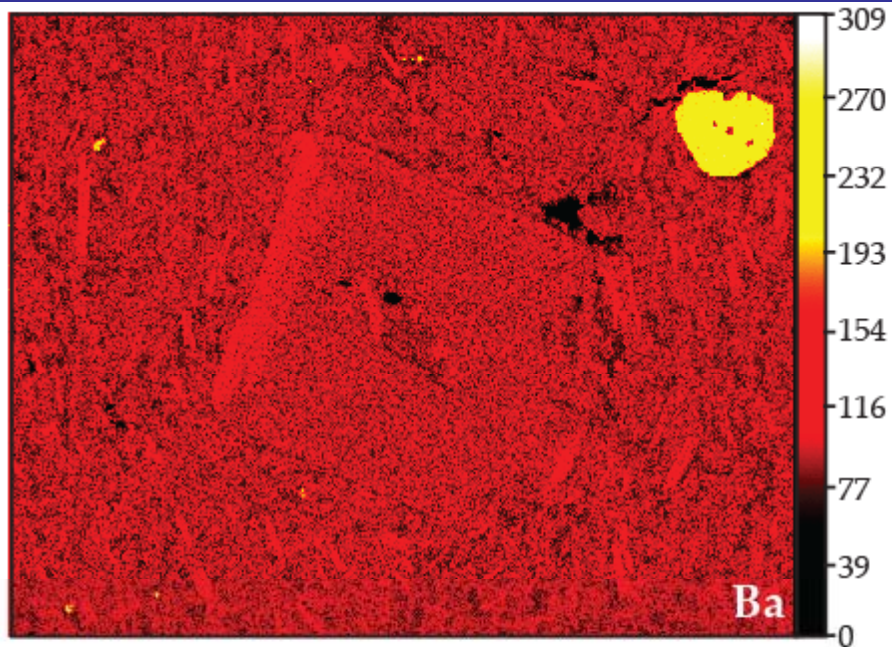
Move crystal and detector to select different X-ray lines



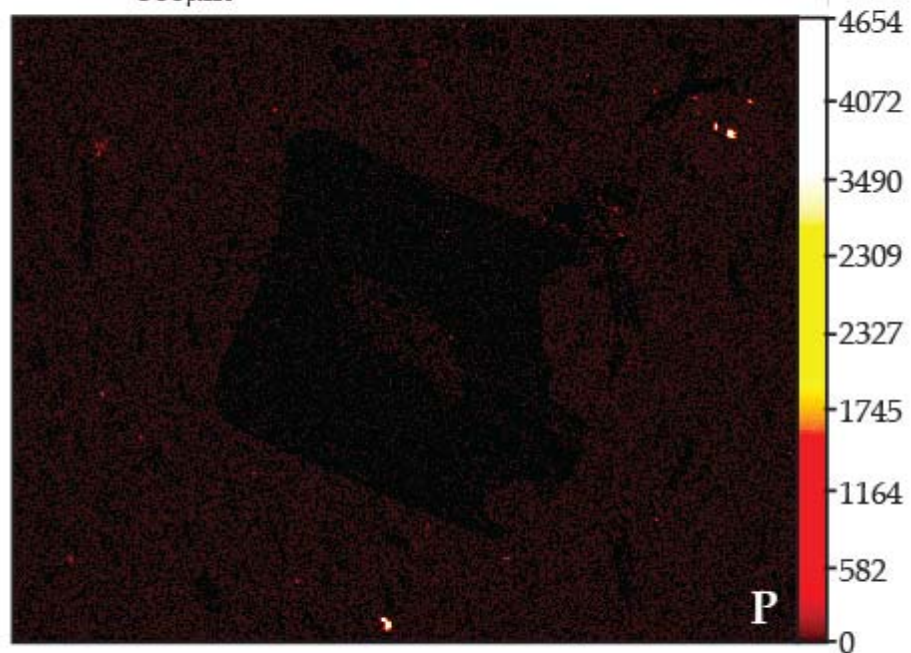
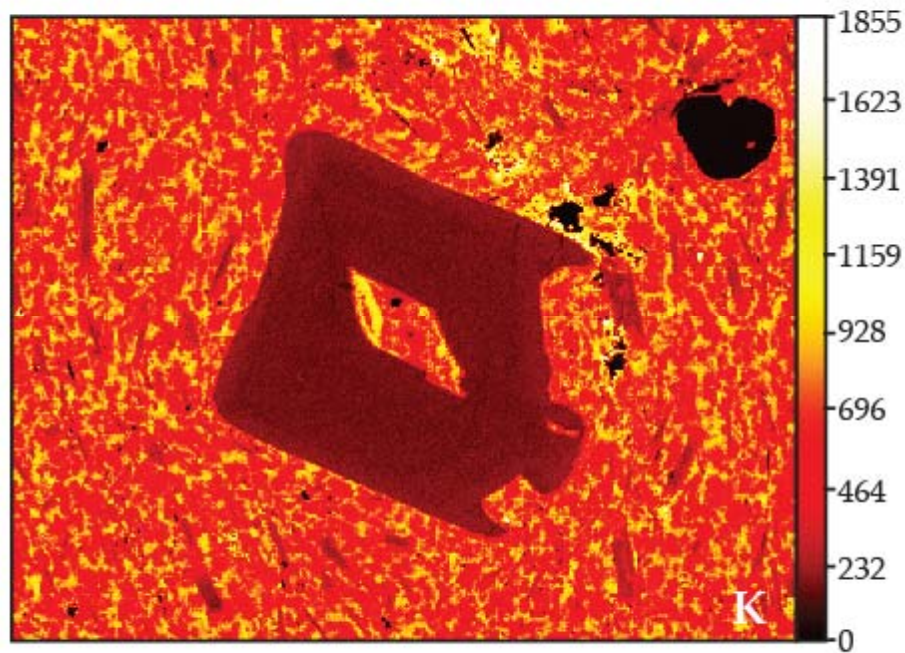
M. Jercinovic, 2007

Chemical Analysis of Minerals





500 $\mu$ m





# SPECTROSCOPIC TECHNIQUES: EPMA & SEM

- Scanning Electron Microscopy (SEM) basics

- 1) Very similar to EPMA in that an electron gun is used to generate and fire electrons in a beam at a sample.

- 2) SEM is generally considered only semi-quantitative, but can produce incredible images using both *secondary electron scatter* or *backscattered electrons* (BSE).

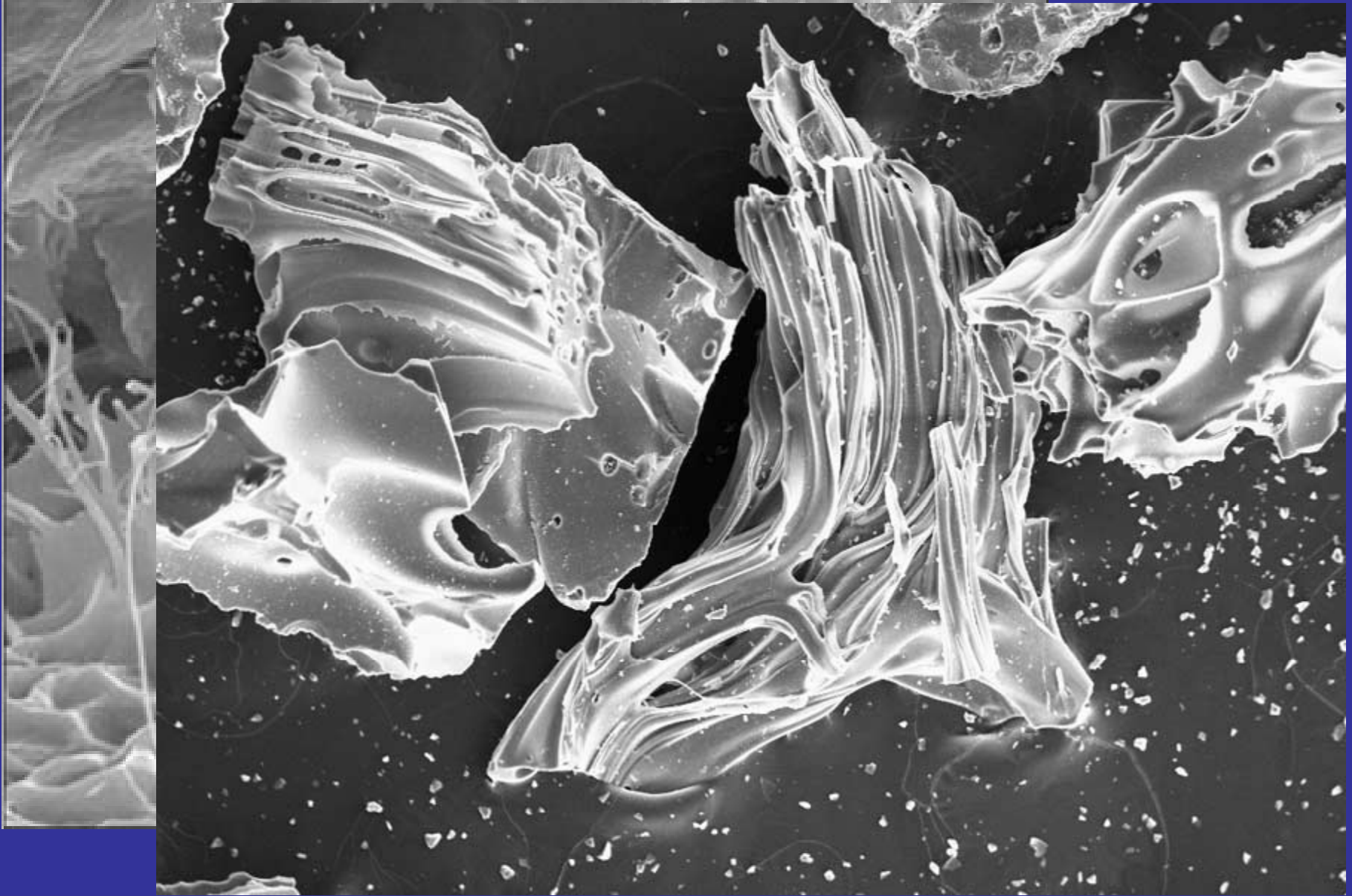
- A) Secondary electron images can reveal a great deal about the topography of a sample.

- B) BSE reveal contrasts based on average atomic number such that images will reveal higher rates of backscatter based the relative density of atoms composing the material.

- 3) EDS spectrometers are most commonly used on SEM equipment while microprobes often used both EDS and WDS.



Secondary electron image of illite



## **SPECTROSCOPIC TECHNIQUES: Sample prep.**

- **Scanning Electron Microscopy (SEM)**

- 1) SEM can be performed on thin sections as well as angular mineral grains as well as carbon based materials

- 2) A conductive coat of platinum or gold is required on top of the specimen to mitigate charging issues when the sample is bombarded with electrons

- **Electron probe microanalysis (EPMA)**

- 1) Sample prep for microprobe work requires a bit more effort. Thin sections must be made and ground to  $\sim 30\mu\text{m}$  thickness then polished to a high gloss through a series (15-20) steps.

- 2) Samples must then be carbon coated and kept under vacuum before being qualitatively or quantitatively analyzed.

- Both of these techniques are quite powerful in that samples do not have to be powdered or dissolved and the analysis is non-destructive.

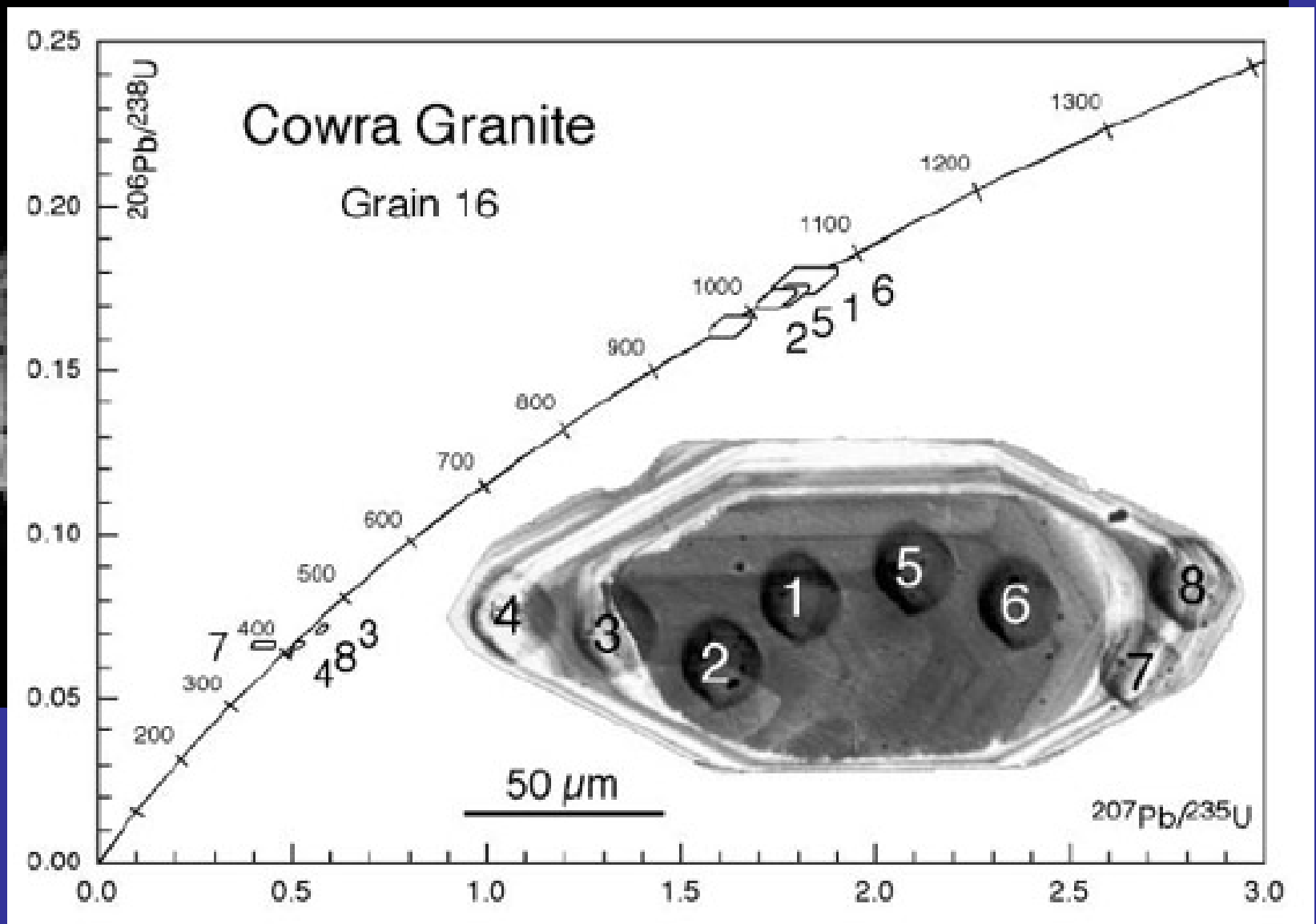
# SPECTROSCOPIC TECHNIQUES: Mass Spec.

- Mass Spectrometry

1) Mass spectrometry analysis comes in a variety of forms. Some common types of mass spec are a) *secondary ion mass spectrometry (SIMS)*, *thermal ionization mass spectrometry (TIMS)*, and *multicollector mass spectrometry*.

2) All these techniques are similar in that an ion beam is generated by a type of plasmatron or an alkali metal. The beam is then focused at a sample and used to erode and sputter the target area. This sputtered and ionized material is then carried into the spectrometer by a counter gas.

- Mass spectrometry can be conducted in-situ, on mineral separates, or dissolved specimen. Mass spec is also very good for analyzing extremely light elements (i.e. H, Be, Li) because the ion beam is relatively low energy so light elements or things of very low abundance can still be counted; therefore, it is very useful for analysis of stable and radiogenic isotopes (i.e. age dating).



# SPECTROSCOPIC TECHNIQUES: PIGE & PIXE

- Photon-Induced Emission Spectroscopy

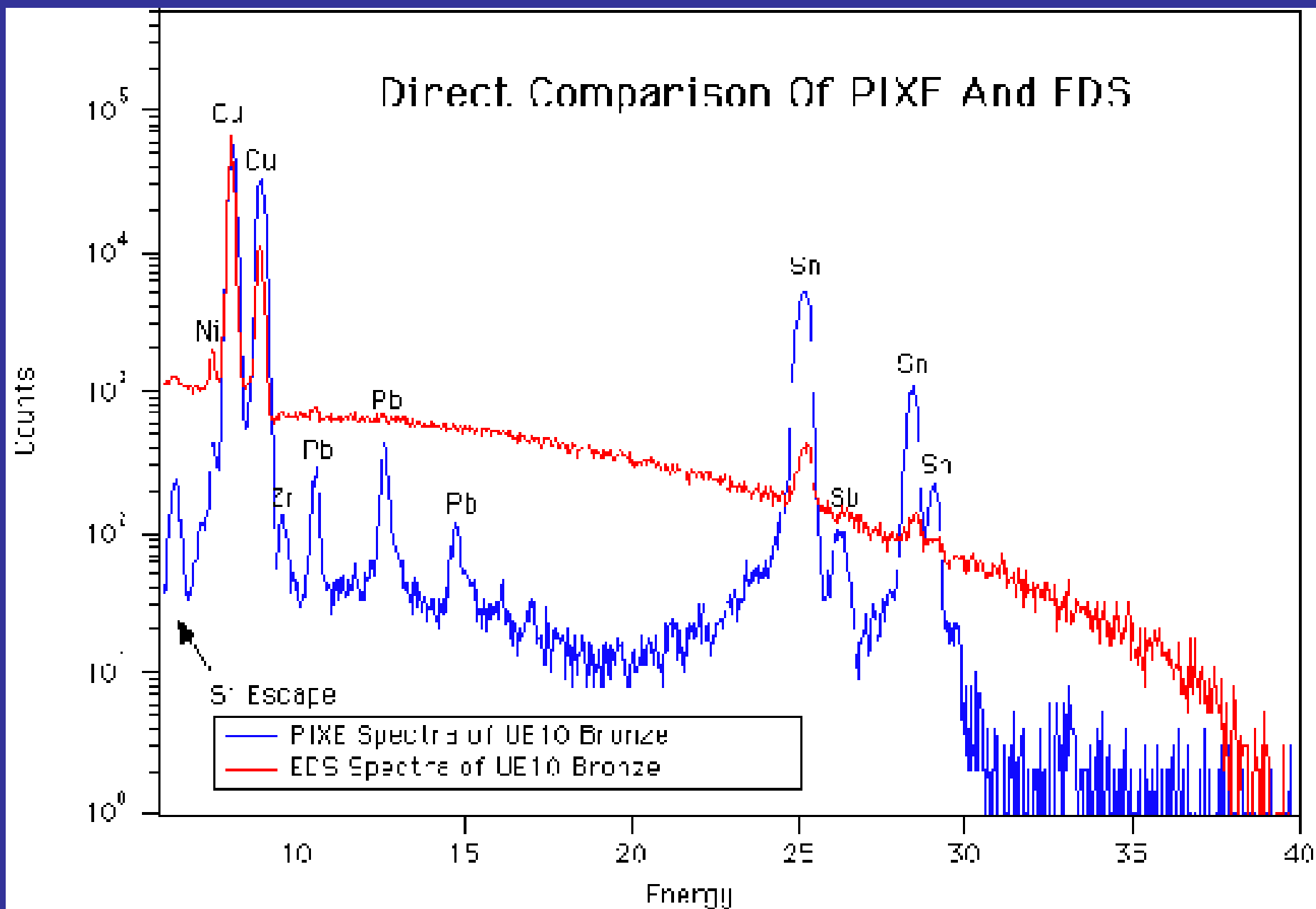
- 1) Broadly, there are two types of photon-induced spectroscopy: *gamma-ray* and *x-ray*

- 2) As opposed to the other types of spectroscopy discussed previously, this technique uses a proton beam at very high energy to produce incredibly small, electro-megnetically focused beams with little to no background interference signal.

- 3) Together *PIGE* and *PIXE* can analyze the entire range of elements by their characteristic x-rays.

- Despite the utility of these techniques, they have been somewhat limitedly applied because the power needs require the use of a nuclear accelerator.

## Direct Comparison Of PIXF And FDS





# SPECTROSCOPIC TECHNIQUES: Neutron Activation

- Neutron Activation Analysis

- 1) There are a wide variety of types of neutron activation analysis. The different types of analysis are based on the half lives of the elements of interest.

- 2) All types of neutron activation analysis are based in the idea that *any* element can be made radioactive if it is bombarded with enough energy.

- A) In this type of spectroscopy, samples are placed in a nuclear reactor where they are targeted by neutrons to generate a thermal flux.

- B) Known standards are placed in the reactor along with the unknown.

- C) Both the sample and the unknown are removed from the reactor together. Immediately, both materials begin to decay and produce gamma radiation that can be counted and used as a proxy for concentration.

# SPECTROSCOPIC TECHNIQUES: Neutron Activation

- Neutron Activation Analysis (types)

1) *Prompt Gamma-Ray* (PGNAA): radioactive nuclides are counted in the reactor as the sample is irradiated. This is useful for elements that have *very* short half lives.

2) *Delayed Gamma-Ray* (DGNAA): radioactive nuclides are counted once the sample and a standard is removed from the reactor over a period of days. In most cases, this technique is the most useful as small volumes of sample can be used to study 25 to 30 (and sometimes more) elements in a single run.

3) *Radiochemical* (RNAA): this is an almost identical technique to DGNAA, but some poor graduate student has to physically separate specific phases after they are irradiated. This is difficult and expensive and unless you have a very specific low abundance isotope that is of great interest, it is not common.

4) *Fast* (FNAA): this technique is similar to PGNAA in that nuclides are counted soon after irradiation, but in this case they are based through a flux source and counter tube.

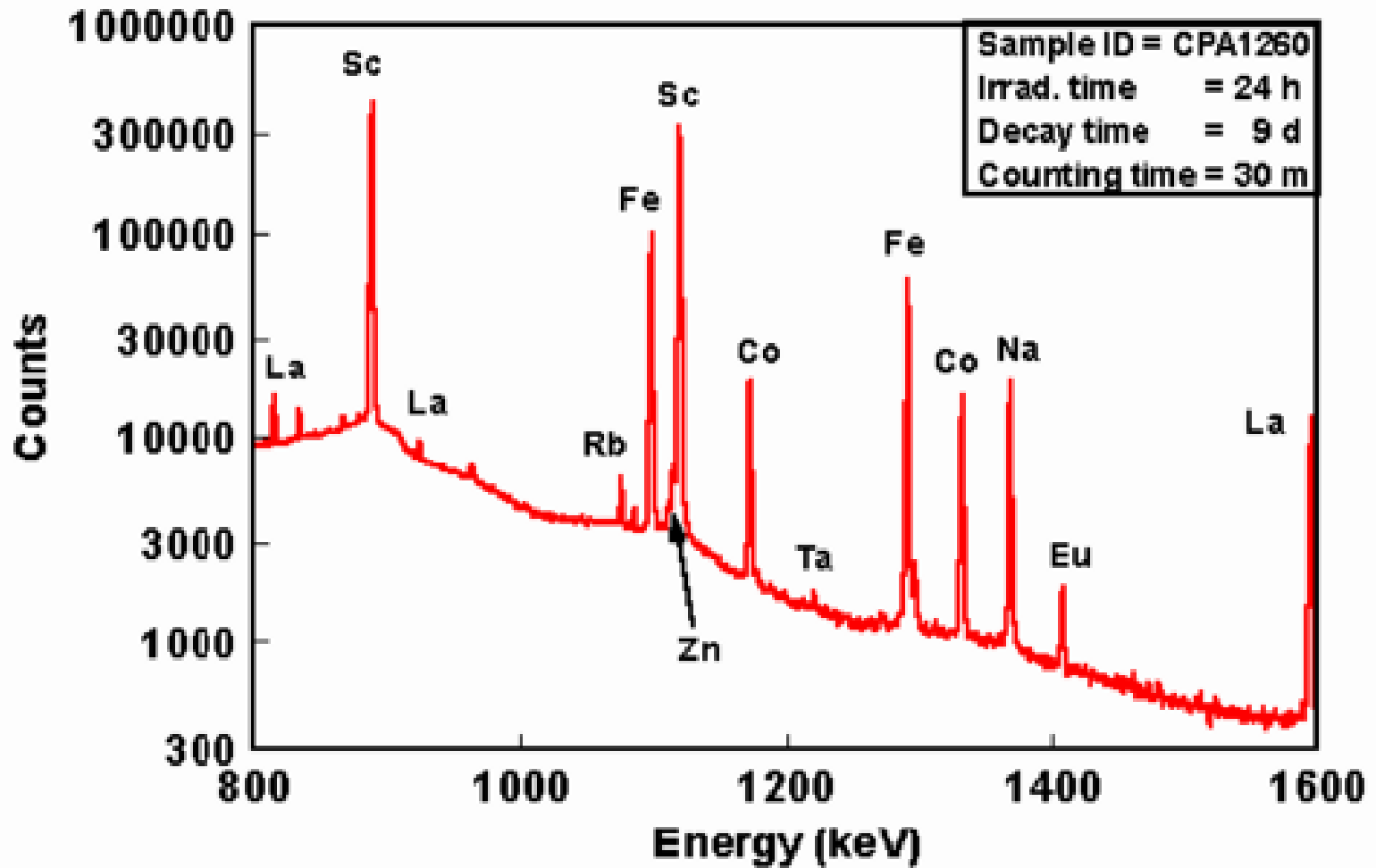
REACTOR LV

Target Nucleus

Prompt Gamma Ray

Beta Particle

Inc Ne



CHANNEL OF IONISATION CHAMBER

BEAM TUBE

PRIMARY CIRCUIT TUBE INLET

PRIMARY CIRCUIT TUBE OUTLET



Chemical Analysis of Minerals

# SPECTROSCOPIC TECHNIQUES: Mössbauer

- Really useful for determining oxidation state

- 1) This approach is really good for understanding the valance state of Fe ( $\text{Fe}^0$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) that is usually related to the amount of water available when a rock is crystallizing.

- 2) Relies on the study of gamma-ray particles generated when a nucleus recoils after emitting energy.

- 3) Spectrum from analysis is defined as an *isomer shift* (difference in electron density between the source and absorber) and *quadrupole splitting* (shift in the nuclear energy level caused by the electron generated electric field gradient).

- 4) These two characteristics are used in combination to identify the valance state and site occupancy of Fe for a specific mineral phase. The problem is that Fe sits in similar sites in a lot of mineral phases, so this technique is only useful once other techniques have been applied to understand the nature of the phase being studied.

## SPECTROSCOPIC TECHNIQUES: Visible & Infrared

- Study of materials based on the light wavelengths that may or may not pass through them

- 1) Can use ultraviolet, mid-infrared, infrared, and far infrared light generated by tungsten-halogen or deuterium light sources.

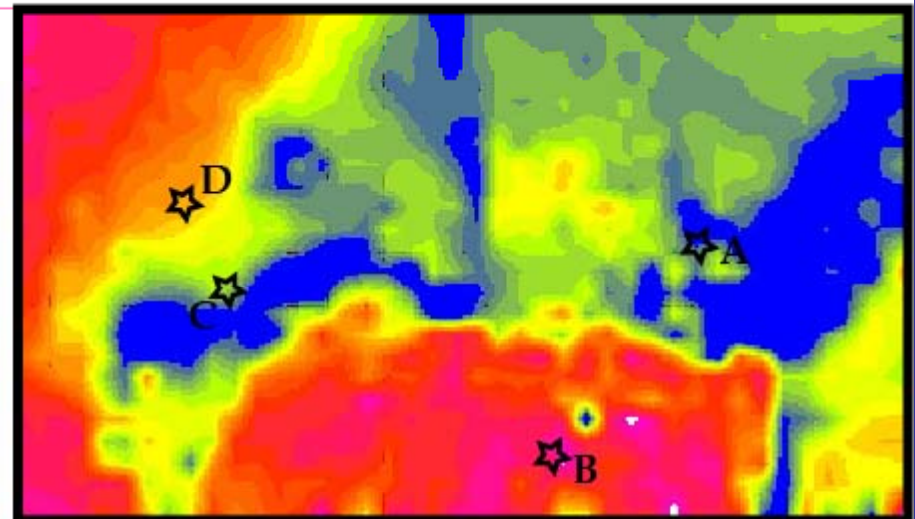
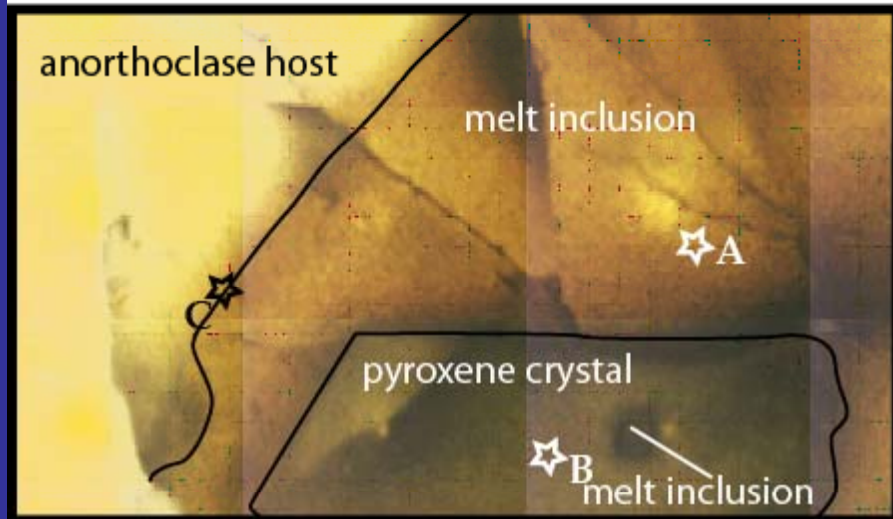
- 2) Light beam is controlled and split to measure air (baseline) and the sample simultaneously.

- 3) Visible light is very useful to study the valance states of transition metals (i.e. Fe, Ti, Cr, Mn, Ni) while infrared light studies are commonly applied to H or C + O species.

- 4) IR spectra are acquired using *Fourier Transform Infrared Resonance* (FTIR) spectroscopy

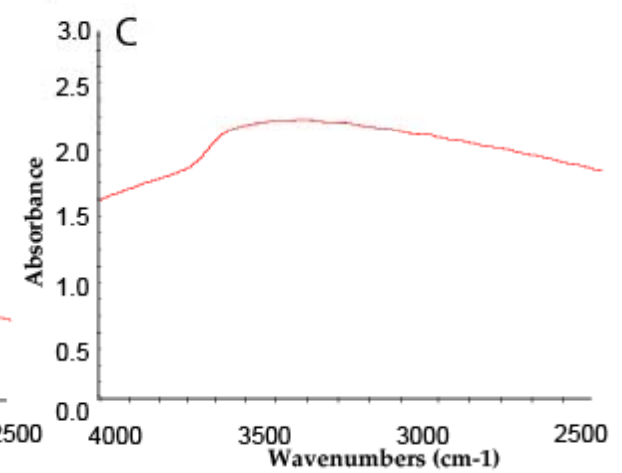
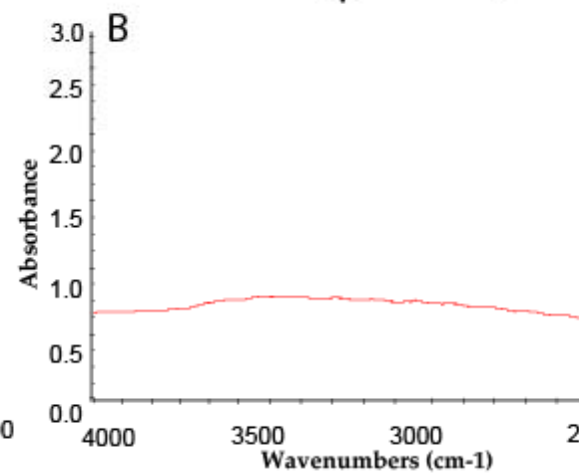
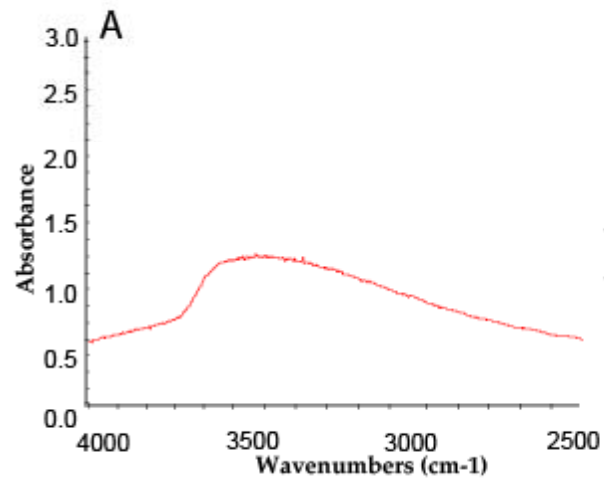
- A) using the known molar absorption coefficient of a particular species, The *Beer-Lambert law* can be applied to calculate concentration of particular species

- B) This law can also be applied to the study of the nature of Si-O and P-O bonds



100 microns

★ location of spectral analysis



## SPECTROSCOPIC TECHNIQUES: Raman

- Raman Spectroscopy is a really good technique to use to identify minerals (even if the grain size is very small or the crystal shape is totally anhedral)

- 1) This technique takes advantage of a fundamental interaction of a photon beam and a target:

- A) Photons can be scattered back off of a target either elastically or in-elastically. For the most part, photons are reflected elastically (*Rayleigh Scattering*); however, inelastic scattering also occurs.

- B) Inelastic scattered photons (*Raman scattering*) typically have a longer wavelength than elastically scattered photons.

- C) The difference in wavelengths is called the *Raman Shift* and is characteristic of specific mineral phases.

- This technique is really helpful in discerning between polymorphs that are otherwise identical using other techniques.

## Concluding Thoughts...

- The chemical analysis of minerals is a critical component to understanding the variety of environments in which rocks form... most of which we have never actually observed!

- That being said, there are a lot of ways to misuse these techniques or get very little out of them.

  - Understanding as much as possible about the mineral(s) you intend to study, their petrogenesis, and host environment is essential before pursuing detailed chemical analysis.

  - All types of chemical analysis can be dangerous if they are treated as black box techniques. There are many instruments out there that can produce great results; however, machines can also produce bad or meaningless results so knowing something about the principals involved in the technique can be very helpful.