

Fundamentals of mudrock chemostratigraphy: Handheld XRF analysis, calibration, and interpretation

GCAGS Short Course

INSTRUCTORS

Harry Rowe

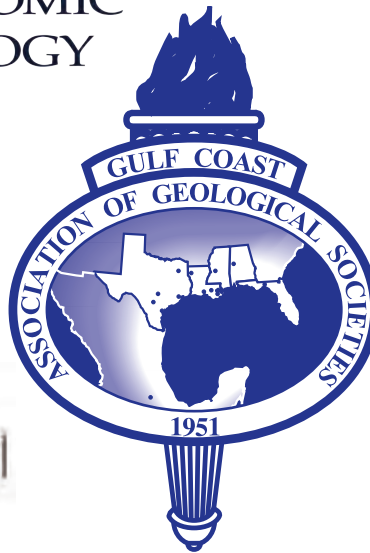
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BUREAU OF
ECONOMIC
GEOLOGY



**Austin, Texas
October 20, 2012**

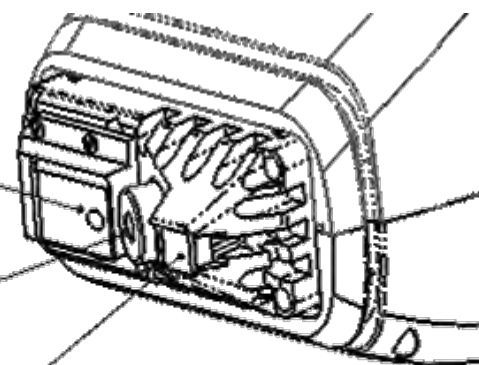
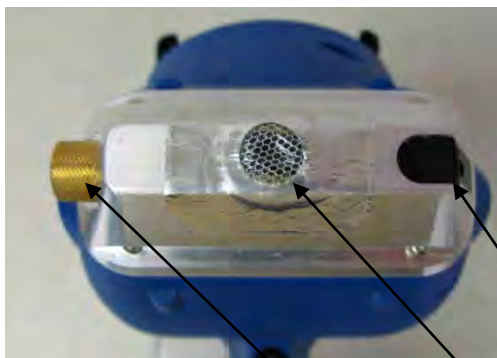
XRF Workshop



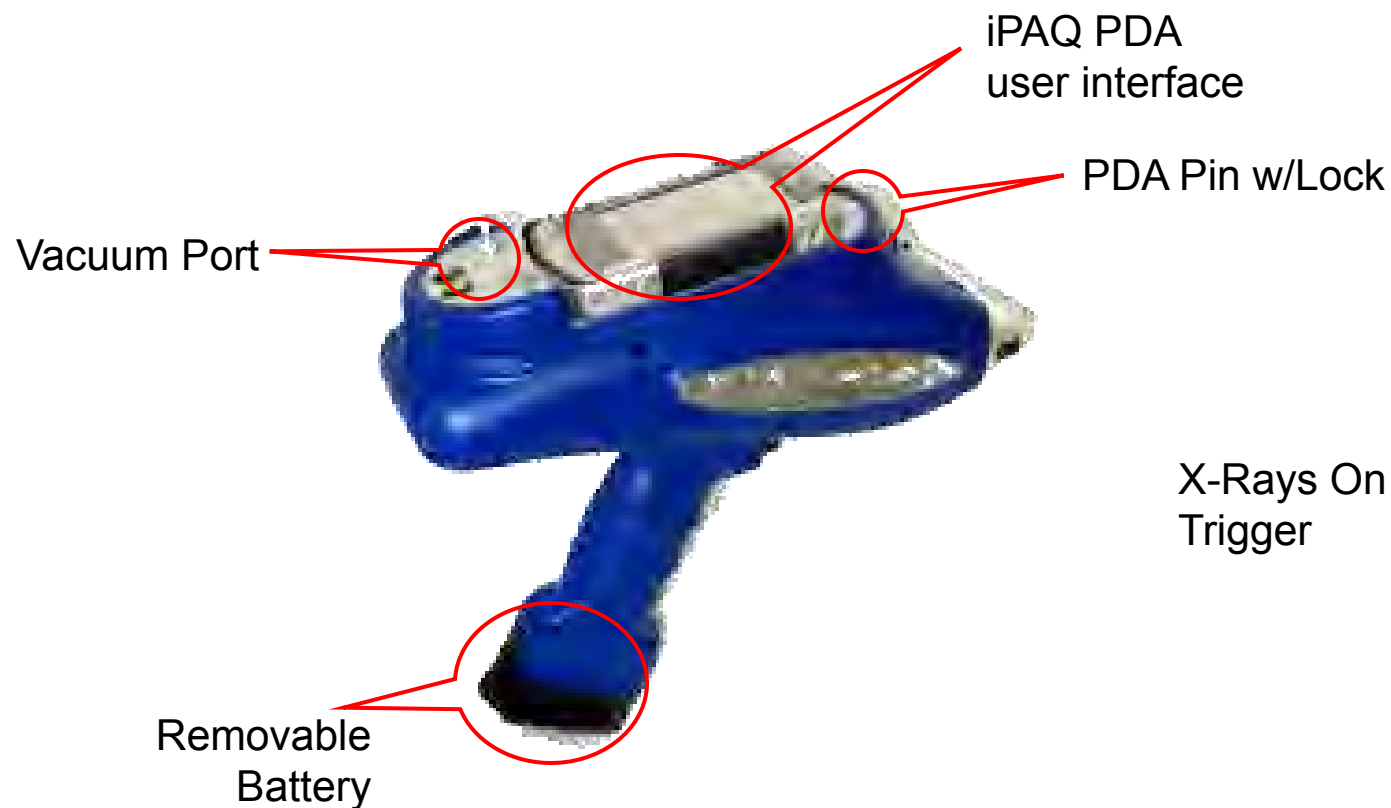
Dr Bruce Kaiser

Instrument – The Basics

- X-ray Tube Ag, Rh or Re Target
- Up to 45kV X rays
- 140eV Resolution Si-Drift Detector
- 13 μ Be Detector Window
- IR Safety Sensor
- Vacuum window
- User selectable filter/target



Instrument – The Basics



How it Works – What is x-ray fluorescence?

In the most basic terms, x-ray fluorescence is the process in which:

- a **photon** is emitted from an x-ray source
- The emitted **photon** interacts with the atoms in the sample
- In some cases, this interaction causes an electron to get “knocked out” of the inner shell of a given atom
- When an electron leaves an inner shell, the atom becomes “unstable” and wants to fill the vacancy, so an electron from a higher shell drops down to fill that vacancy
- When an electron drops from a higher to a lower shell, a certain energy is released in the form of another **photon**, which is characteristic not only to each element, but to each shell transition; this is fluorescence
- In x-ray fluorescence instruments, a detector is used to pick up the characteristic fluorescent energies.

We'll get into further details of XRF once we further explore photons.

Good news: you already know a lot about photons!

How it Works – Photons

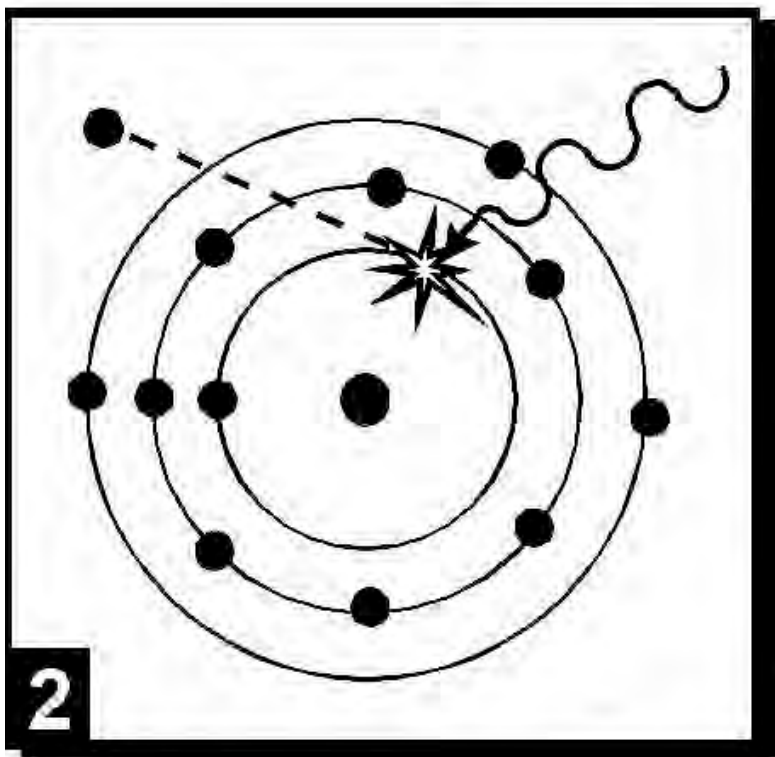
What is a photon?

While nobody know exactly what a photon is, we do know:

- “Discrete packets of electromagnetic radiation”
- Force carriers
- Sometimes they exhibit the characteristics of a wave, sometimes the characteristics of a particle
- Have no mass
- Have electromagnetic energy
- Have momentum
- In free space it is thought they always move at the speed of light, c , and consequently in our frame of reference they are infinitely short; i.e. they have no length in the direction they travel
- Appear to be “slowed down” when moving through matter, or absorbed completely

What happened to the good news? Here it comes...

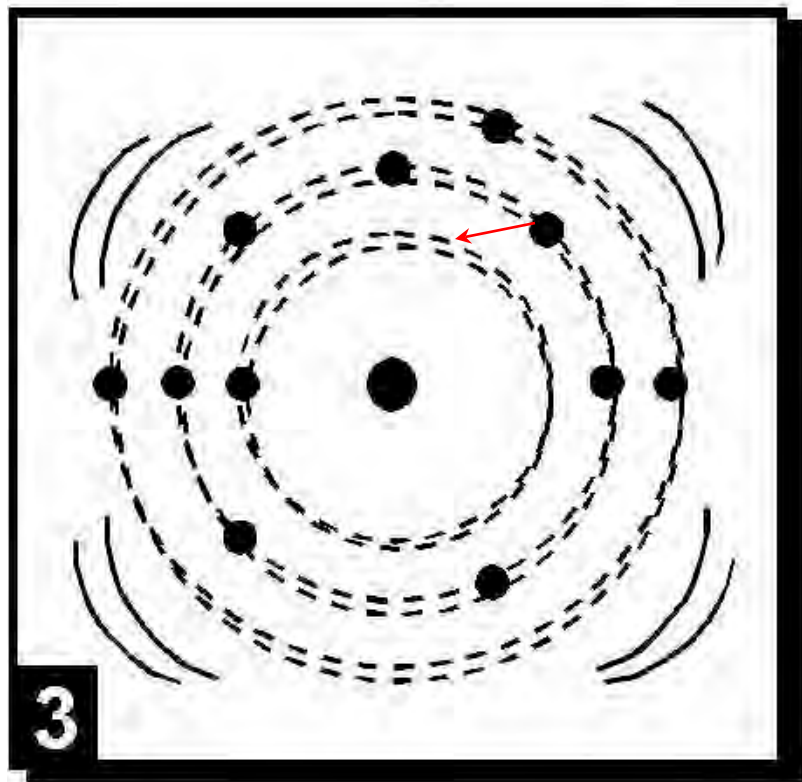
How it Works – XRF (x-ray fluorescence)



When the switch is pulled, activating the Analyzer's x-ray tube, the x-rays strike the inner shell electron of the atoms in the sample and it is ejected from the atom.*

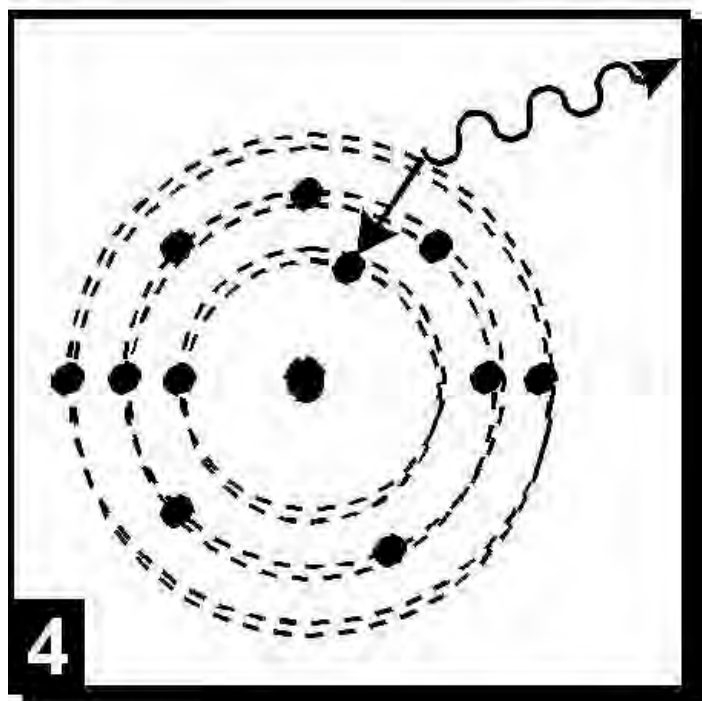
* X-ray energy must be higher than absorption edge of the element.

How it Works – XRF (x-ray fluorescence)



Next, an electron from an outer shell moves to fill the vacancy in the inner shell.

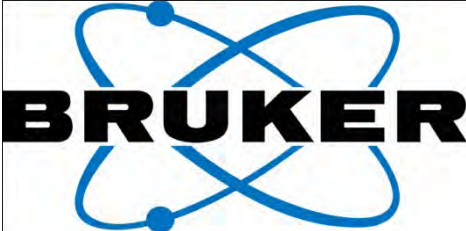
How it Works – XRF (x-ray fluorescence)



An X-ray photon is released and hits the analyzer's SiPIN detector. (This photon's energy is unique to the element it came from-- e.g., Aluminum K-shell energy is 1.47 keV)

Note: Each Element has its Own Signature Energy for K and L-Shell Electrons.



H 1 Hydrogen	Key To Energy Values																B 5 Boron	C 6 Carbon	N 7 Nitrogen
Li 3 Lithium	Be 4 Beryllium															Al 13 Aluminum	Si 14 Silicon	P 15 Phosphorus	
Na 11 Sodium	Mg 12 Magnesium	K 19 Potassium	Ca 20 Calcium	Sc 21 Scandium	Ti 22 Titanium	V 23 Vanadium	Cr 24 Chromium	Mn 25 Manganese	Fe 26 Iron	Co 27 Cobalt	Ni 28 Nickel	Cu 29 Copper	Zn 30 Zinc	Ga 31 Gallium	Ge 32 Germanium	As 33 Arsenic			
Rb 37 Rubidium	Sr 38 Strontium	Y 39 Yttrium	Zr 40 Zirconium	Nb 41 Niobium	Mo 42 Molybdenum	Tc 43 Technetium	Ru 44 Ruthenium	Rh 45 Rhodium	Pd 46 Palladium	Ag 47 Silver	Cd 48 Cadmium	In 49 Indium	Sn 50 Tin	Sb 51 Antimony					
Cs 55 Cesium	Ba 56 Barium	La 57 Lanthanum	Hf 72 Hafnium	Ta 73 Tantalum	W 74 Tungsten	Re 75 Rhenium	Os 76 Osmium	Ir 77 Iridium	Pt 78 Platinum	Au 79 Gold	Hg 80 Mercury	Tl 81 Thallium	Pb 82 Lead	Bi 83 Bismuth					
Fr 87 Francium	Ra 88 Radium	Ac 89 Actinium	Rf 104 Rutherfordium	Ha 105 Hahnium	Sg 106 Seaborgium	Ns 107 Nilsborium	Hs 108 Hassium	Mt 109 Meitnerium	Uun 110 Ununilium	Uuu 111 Unununium	Element 112	113							

K-shell Aluminum
1.48 keV

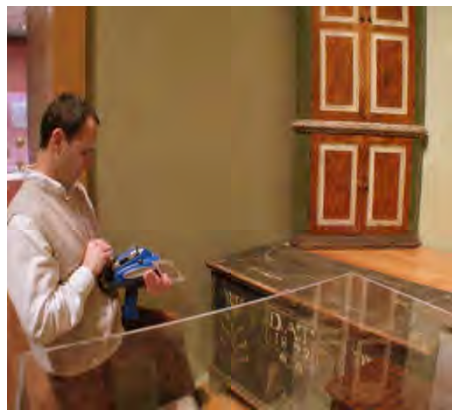
K-shell Iron (Fe)
6.40 keV

Ce 58 Cerium	Pr 59 Praseodymium	Nd 60 Neodymium	Pm 61 Promethium	Sm 62 Samarium	Eu 63 Europium	Gd 64 Gadolinium	Tb 65 Terbium	Dy 66 Dysprosium	Ho 67 Holmium	Er 68 Erbium
Th 90 Thorium	Pa 91 Protactinium	U 92 Uranium	Np 93 Neptunium	Pu 94 Plutonium	Am 95 Americium	Cm 96 Curium	Bk 97 Berkelium	Cf 98 Californium	Es 99 Einsteinium	Fm 100 Fermium

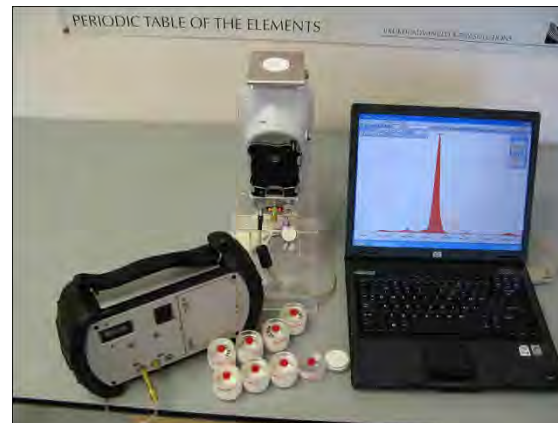
Lanthanide Series

Actinide Series

How It Works - XRF



In the Field

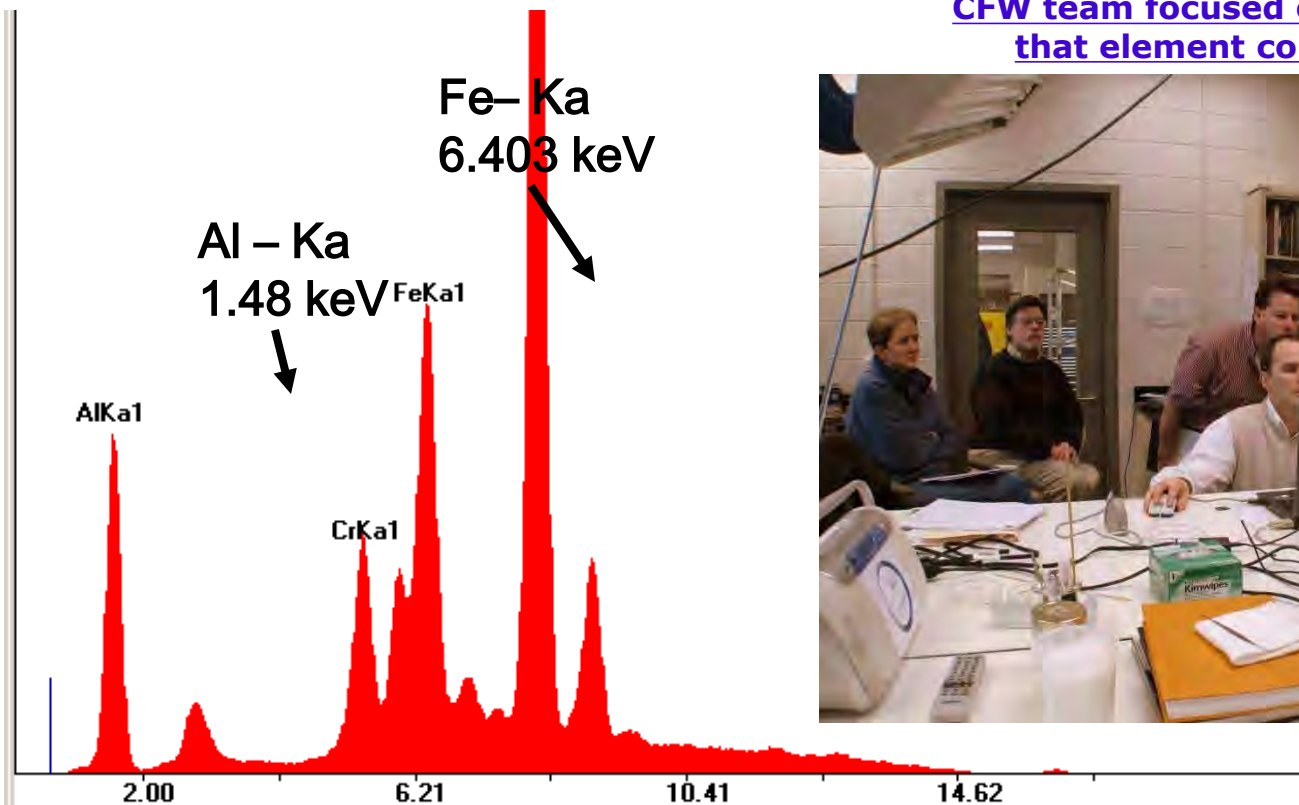


Very sensitive elemental analysis by anyone in seconds anywhere

The signal passes from the instrument's SiPIN Detector to the digital pulse processor, then to the CPU where the data is transformed from counts per channel, to spectra and quantitative chemistries in seconds with no sampling .

Each Element has its Own Signature Energy for K and L Electron Shells.

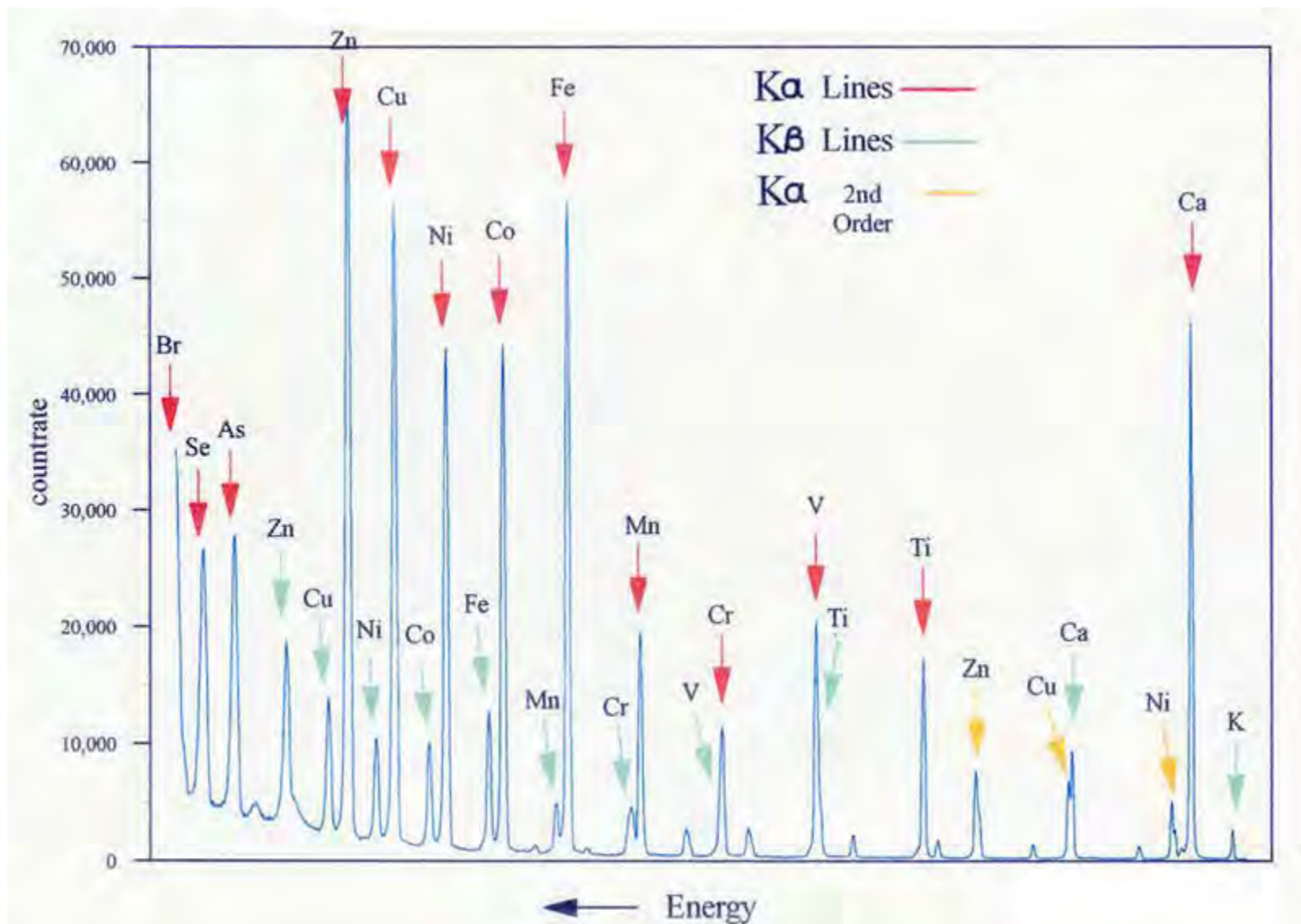
CFW team focused on "where did that element come from?"



Data Evaluation – Reading Spectra

- The spectrum is your raw data, what the detector sees when you shine your flashlight. It never lies.
- For each element you think you see, you should be able to find an alpha and a beta peak (very trace amounts can be an exception to this rule)
- Each element has a variety of possible fluorescence peaks
- Some of these peaks will overlap
- A higher peak does not necessarily mean a higher concentration
- There are some special cases, such as sum peaks, instrument artifacts, etc.

Data Evaluation – Reading Spectra



Data Evaluation – Reading Spectra

What all this about K,L,M, alpha, and beta?

The energy of an X-ray corresponds to the difference in energy of the energy levels concerned. K-fluorescence is the term given to the fluorescence that occurs when replenishing the K-shell, L-fluorescence to that released when replenishing the L-shell etc.

Also needed for the full labeling of the emitted X-ray line is the information telling us which shell the electron filling the "hole" comes from. The Greek letters α , β , etc. are used for this with numbering to differentiate between the various shells and sub-levels.

Data Evaluation – Reading Spectra

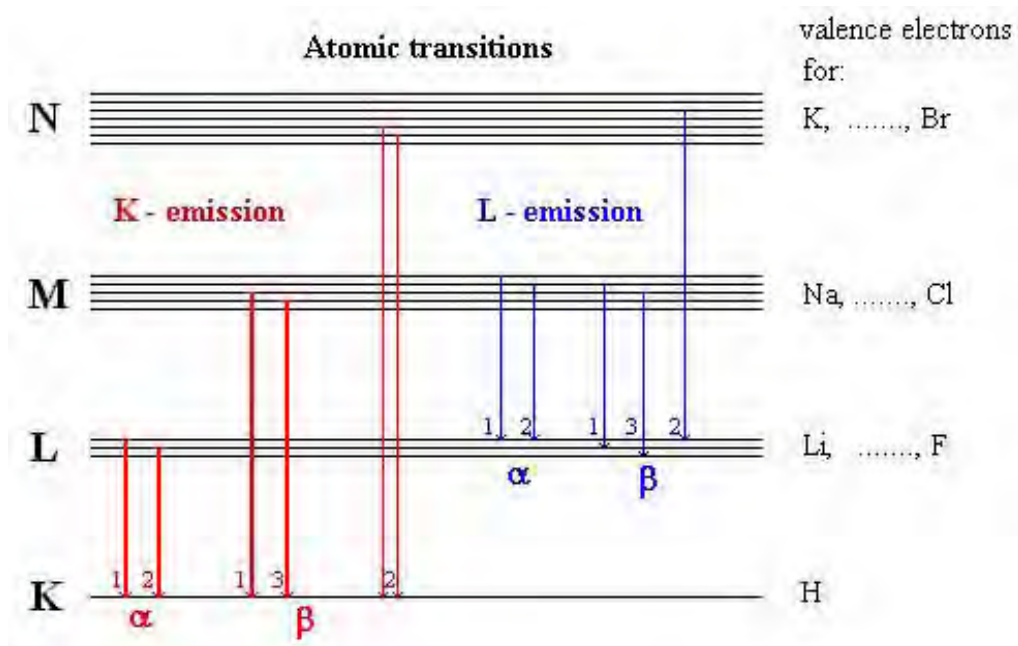


Fig. 2: X-ray line labeling

Examples:

$K\alpha_1$ Electron from sub-level L_{III} to the K-shell

$K\alpha_2$ Electron from sublevel L_{II} to the K-shell

$K\alpha_{1,2}$ if neither line is resolved by the spectrometer

$K\beta_1$ Electron from sublevel M to the K-shell

$L\alpha_1$ Electron from sublevel M to the L-shell

Data Collection - Considerations

- What am I really analyzing?
 - Homogeneity
 - Depth of attenuation
- Layers?
- Number of points/samples?
- Define what you want to know.

Depth of Attenuation

A common question: “how deep am I analyzing?”

Answer: it varies a great deal. The depth from which a signal can make it back to the detector is highly dependent on both the density of the sample matrix and the element of interest.

As a general rule of thumb:

- The “lighter” the matrix, the deeper from within the sample can a returning fluorescent energy make it to the detector.
- The “heavier” the element of interest, the deeper from within the sample can its returning fluorescent energy make it to the detector.

The Math:

Depth of Attenuation = $4.61 / (\rho \times \mu/\rho)$

4.61 = natural log of 1/100

ρ = density of matrix

μ/ρ = mass attenuation coefficient

**A table of mass
attenuation coefficients
can be found at:**

<http://www.nist.gov/pml/data/xraycoef/index.cfm>

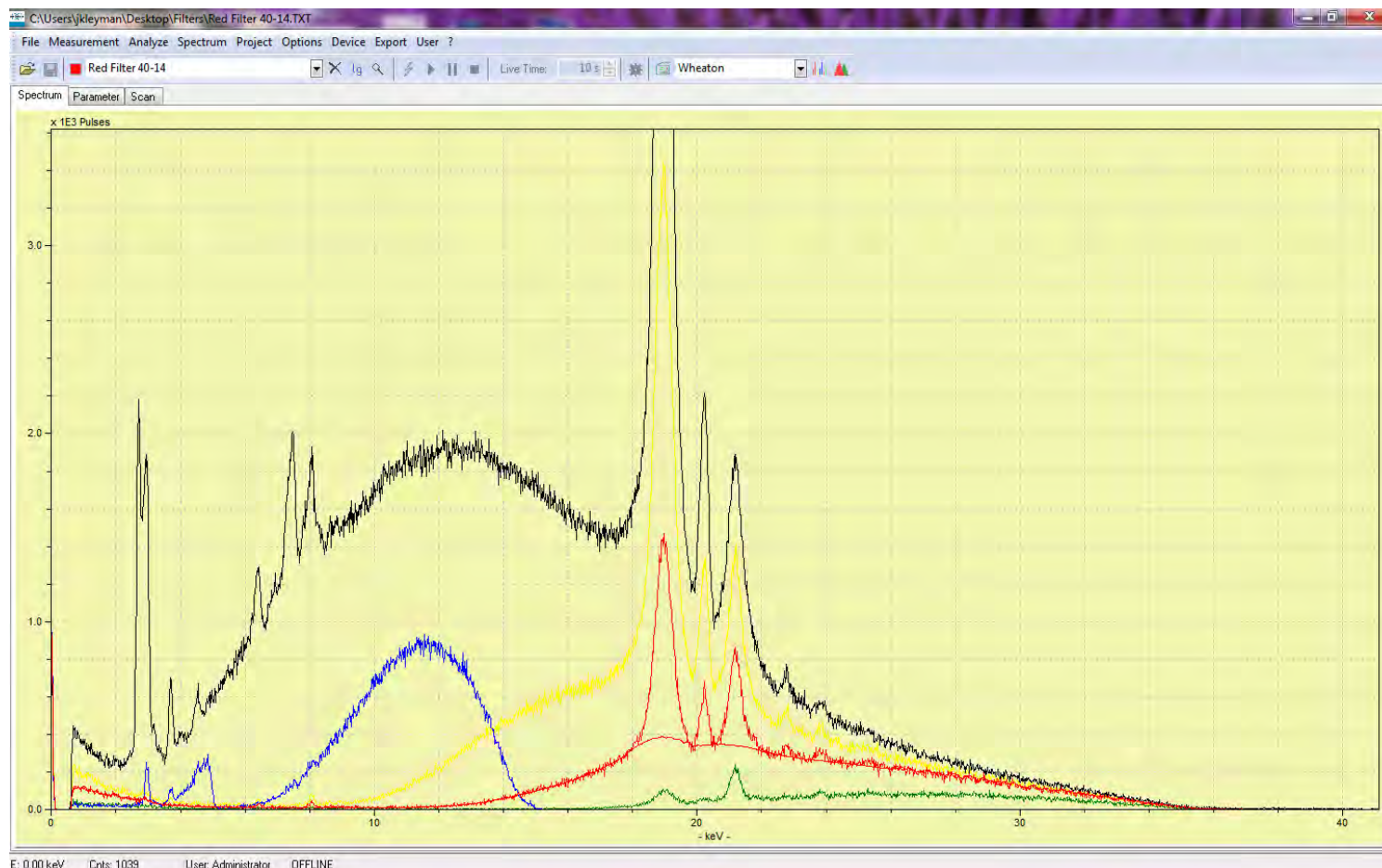
Instrument Set-Up – Getting Started

In the Workshop Folder you will find the Tracer Startup Guide—"Must Do Tracer III-V+ and SD systems." Follow it step-by-step! Don't skip steps!

On the instrument:

- Remove the PDA from the instrument.
- If doing low mass elements (elements from Mg to Cl) connect vacuum system, it should read below 15 on the gauge. If not Replace Vacuum window.
- Connect the computer to instrument with serial cable (and USB adaptor if no serial port on computer). Note, you must have the driver for the serial cable installed.
- Insert battery or connect instrument to AC power.
- Insert power key and turn instrument on (note, yellow light should come on)
- Cover IR safety sensor on nose of instrument next to vacuum window. Wait 1 minute before bring up software on computer

Data Collection – Filter/Voltage/Current Choice



The different “color” filters produce different signals, or beams, or Bremstrahlung continuums. Why?

Data Collection – Filter/Voltage/Current Choice

To optimize for particular elemental groups, one wants to use filters and settings that “position” the X ray energy impacting the sample just above the absorption edges of the element(s) of interest. The tube current setting is to just optimize the RAW COUNTRATE in the detector so it is between 1000 and 10,000. It should be adjusted to meet this requirement.

Screening for all Elements (Lab Rat mode):

1. No filter
2. 40 kV
3. Highest available micro amps (for non metallic samples)
4. Lowest available micro amps (for metallic samples)
5. Utilize the vacuum.

These settings allow all the x rays from 1 keV to 40 keV to reach the sample thus exciting all the elements for Mg to Pu, although not optimally. Not ideal for trace elements.

Data Collection – Filter/Voltage/Current Choice

Measurement of Silicate or Ceramic materials for higher Z elements (Rb, Sr, Y, Zr, and Nb):

1. 0.006” Cu, .001” Ti, .012 Al Filter (**green filter**)
2. 40 kV
3. Highest current setting available
4. No vacuum

These settings allow all the x rays from 17 keV to 40 keV to reach the sample thus efficiently exciting the elements from Fe to Mo. These are some of those key to identifying the origin of obsidian. There is little or no sensitivity to elements below Fe with these settings.

Data Collection – Filter/Voltage/Current Choice

Measurement of Mg, Al, Si and P to Cu (and any L and M lines for the elements that fall between 1.2 and 8 keV)

1. No filter
2. 12 to 15 kV
3. Highest current setting available
4. Vacuum

These settings allow all the x rays from the tube up to 15 keV. In particular this allows the Rh L (2.5 to 3 keV) lines from the tube to reach the sample. These are particularly effective at exciting the elements with their absorption edge below 2.3 keV. Note this set up is **not good for Cl and S detection, as the scattered Rh L lines interfere with the x rays coming from these elements.**

Data Collection – Filter/Voltage/Current Choice

Measurement of Mg, Al, Si, P, **Cl, S**, K, Ca, V, Cr, and Fe (and any L and M lines for the elements that fall between 1.2 and 6.5keV)

1. Ti filter (*blue Filter*)
2. 15 to 20 kV
3. Highest current setting available
4. Vacuum

These settings allow x-rays from 3 to 12 keV to reach the sample. In particular this does **not allow the Rh L lines from the tube to reach the sample. These Rh L x rays would interfere with Cl and S analysis. For example, this is a very good set up for measuring Cl on the surface of Fe.**

Data Collection – Filter/Voltage/Current Choice

Measurement of metals (Ti to Ag K lines and the W to Bi Lines):

1. 0.001” Ti, .012 Al (*Yellow filter*)
2. 40 kV
3. Lowest current setting (monitor the count rate)
4. No vacuum

These settings allow all the x rays from 12 keV to 40 keV to reach the sample thus efficiently exciting the elements noted above. These are the settings used to calibrate the system for all modern alloys of those elements of those listed in the title of this section. There is little or no sensitivity to elements below Ca with these settings.

Data Collection – Filter/Voltage/Current Choice

Measurement of Poisons (higher Z elements Hg, Pb, Br, As):

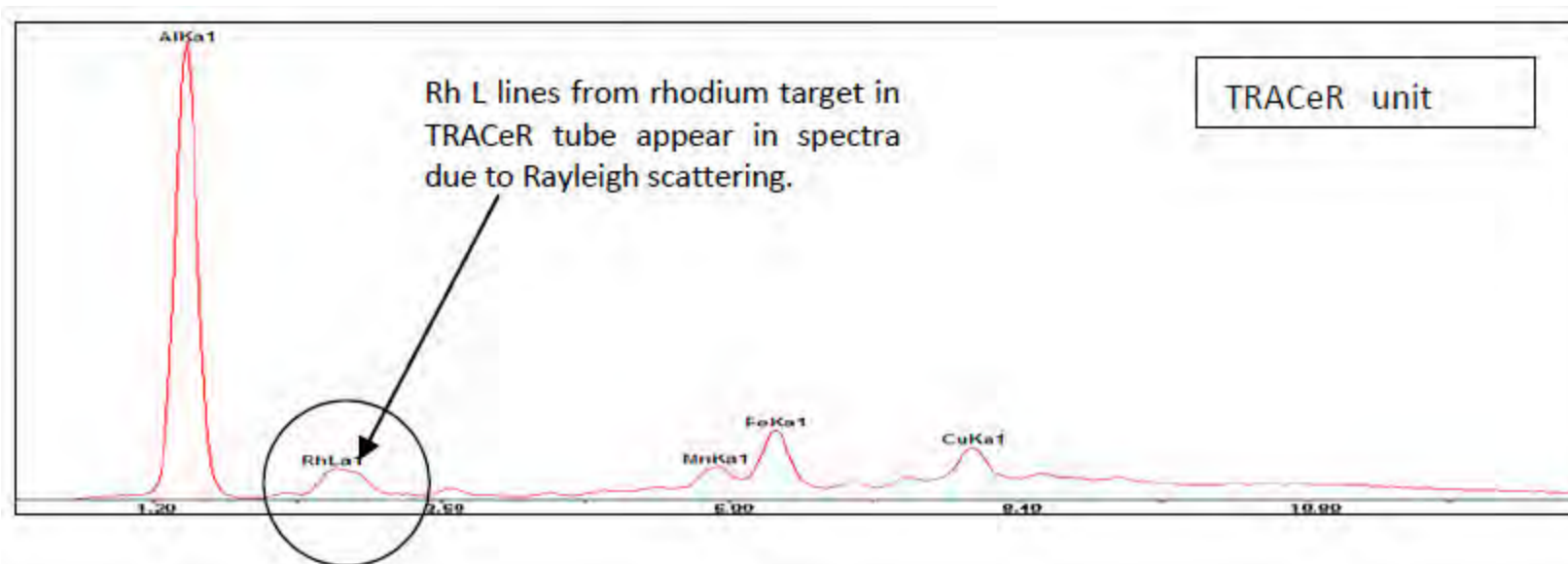
1. 0.001" Cu, .001" Ti, .012 Al (*Red Filter*)
2. 40 kV
3. Highest current setting available
4. No vacuum

These settings allow all the x rays from 14 keV to 40 keV to reach the sample thus efficiently exciting the elements Hg, Pb, Br, As. These are some of the key elements that were used to preserve organic based artifacts. There is little or no sensitivity to elements below Ca with these settings.

Data Evaluation – Reading Spectra

Rayleigh (Elastic) Scattering

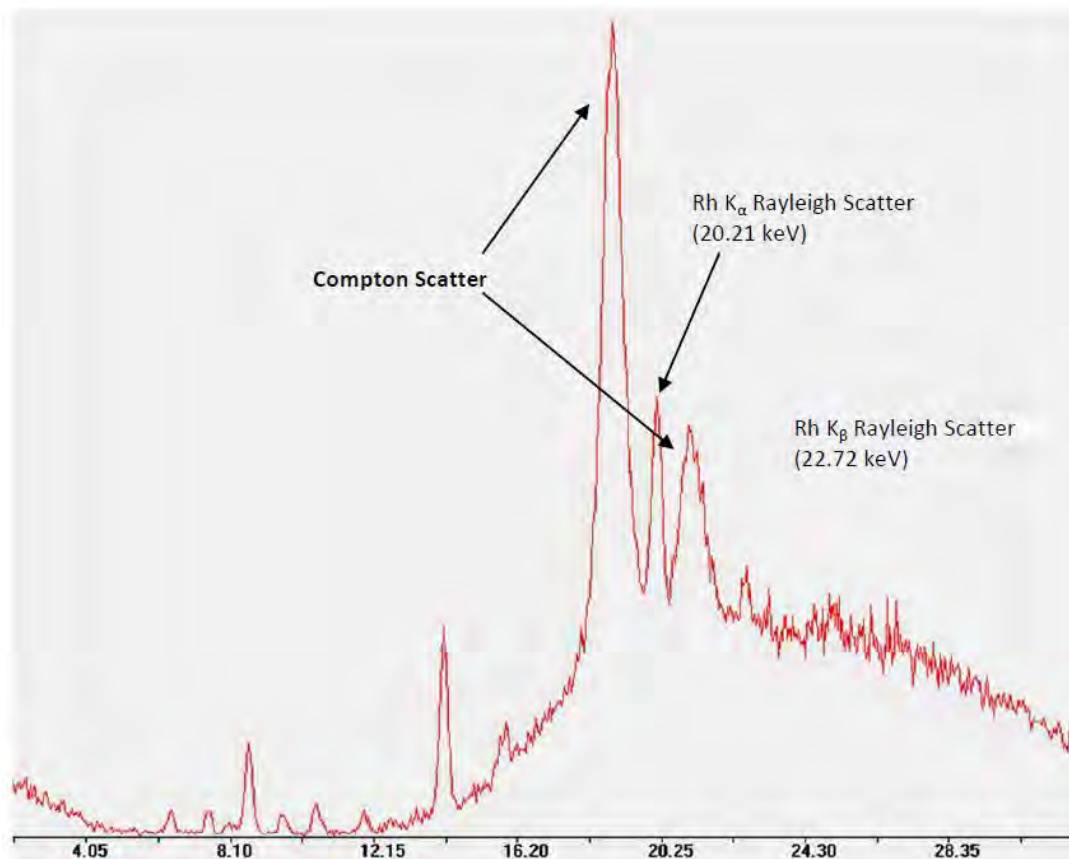
Incident radiation from the tube that reaches the sample is either absorbed in the photoelectric effect or reflected and scattered. When an x-ray reflects off the atoms of the sample without losing any energy it is called Rayleigh (or elastic) scattering. The energy of the outbound x ray will be equal to the energy of the inbound x ray, thus being detected as a source peak with the energy of the inbound x ray. The Rayleigh scatter peaks visible correspond with the characteristic energies of the x-ray tube target element.



Data Evaluation – Reading Spectra

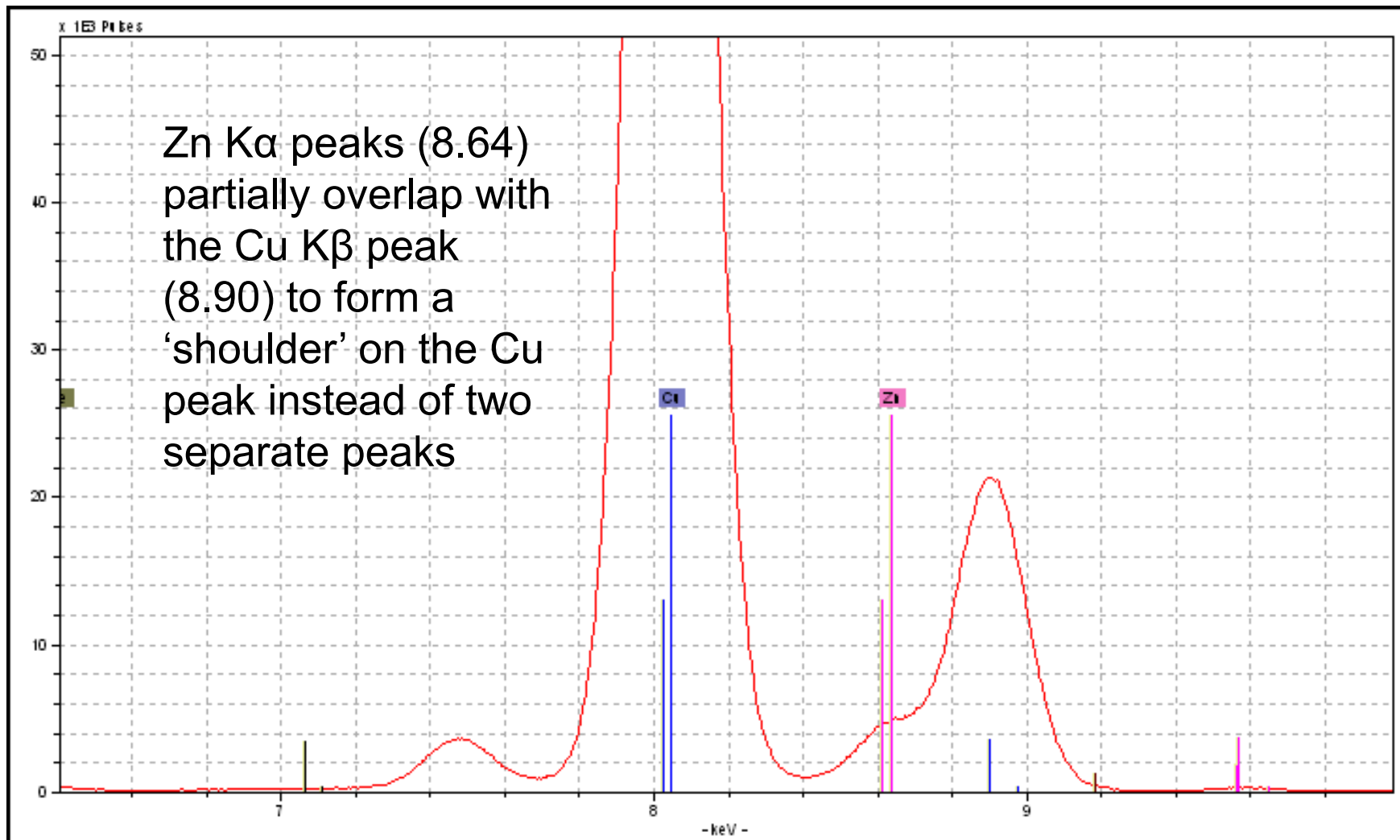
Compton (Inelastic) Scattering

Incident radiation with sufficient energy to ionize an inner-shell electron in an atom does not always cause fluorescence, but instead causes an excitation without losing all of its energy. In these interactions, called Compton scattering, a x ray strikes an atom and loses energy, causing the excitement of an inner-shell electron. Because no vacancy is created in the atom, no characteristic energy is released; however, the x ray will lose energy and be scattered in all directions. Compton scatter x-rays appear as a broad peak defined by the angle between the incident beam and the detector for the target characteristic x-ray lower in energy than Rayleigh scatter peaks because they only lose a small amount of energy in the excitation of an electron. They are generally broad due to the area of the detector and the area of the exciting beam.



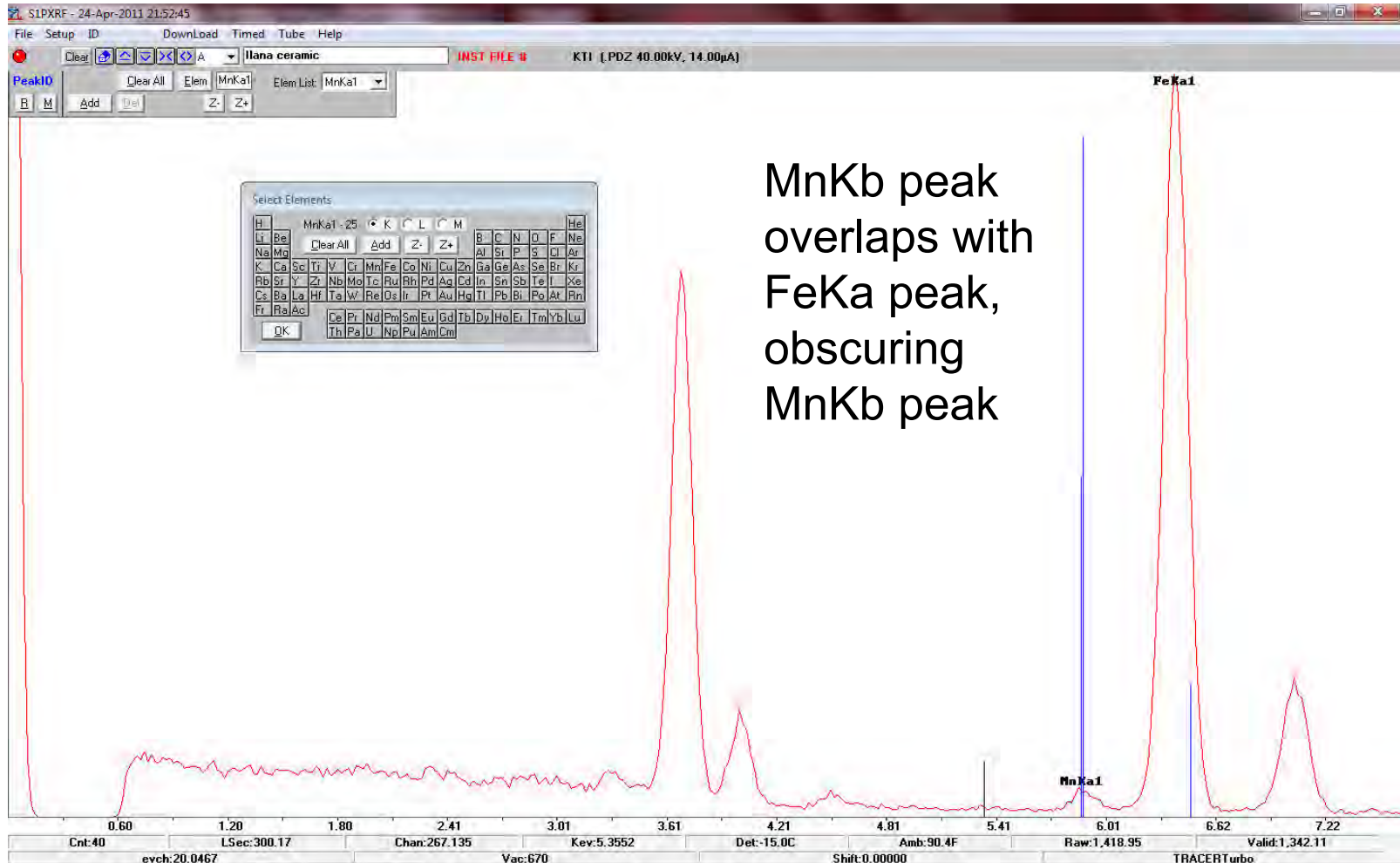
Data Evaluation – Reading Spectra

Peak Overlaps



Data Evaluation – Reading Spectra

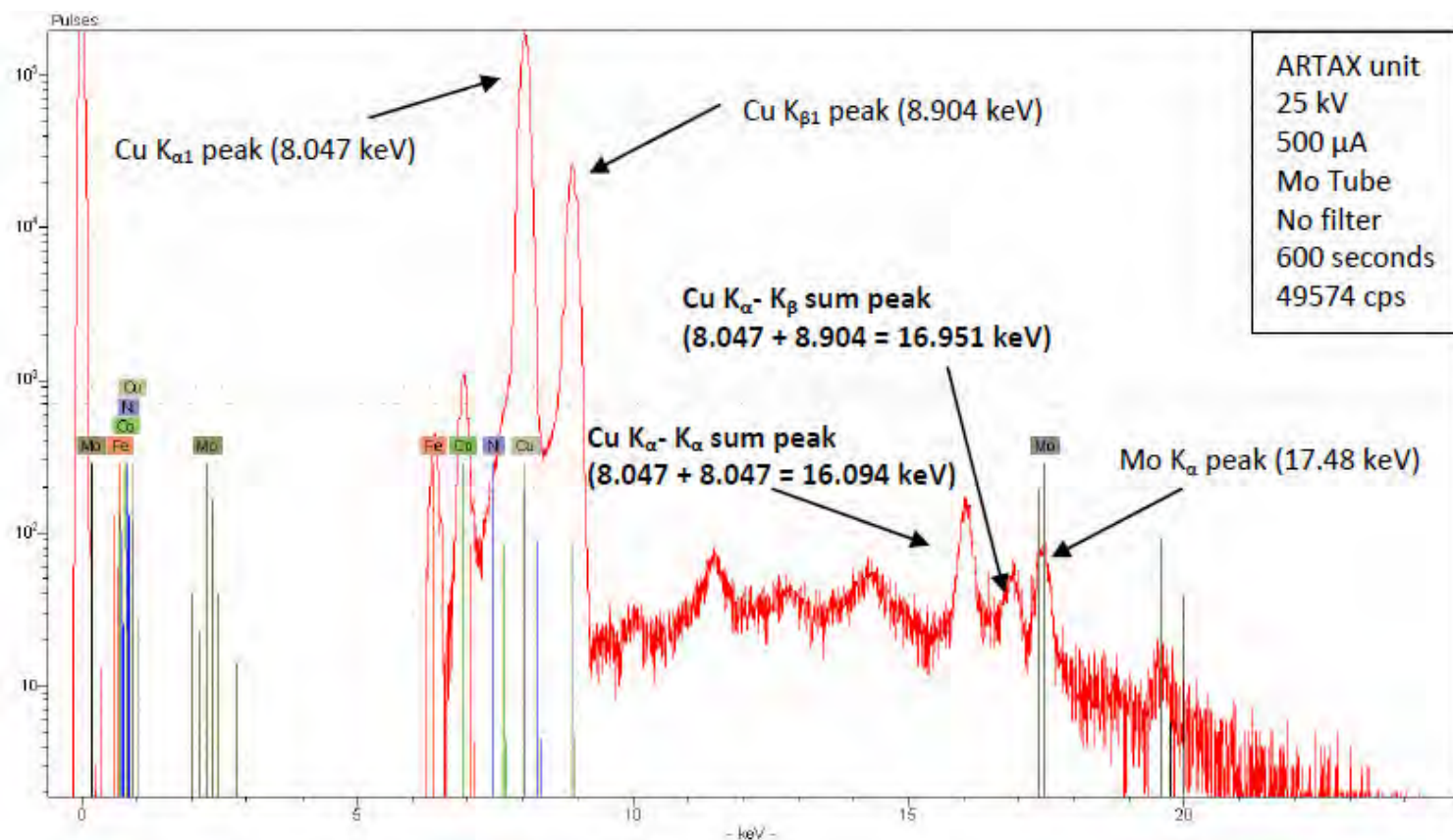
Peak Overlaps



Data Evaluation – Reading Spectra

Sum Peaks

When two or more x rays enter the detector at the exact same time they are read and converted into one pulse with energy equal to the two pulses combined. Sum peaks appear on a spectrum when this occurs enough times to create a visible peak. In theory, sum peaks can appear in any combination of characteristic energies, but they are most commonly found as double K_{α} - K_{α} , K_{α} - K_{β} and K_{β} - K_{β} .



Data Evaluation – Reading Spectra

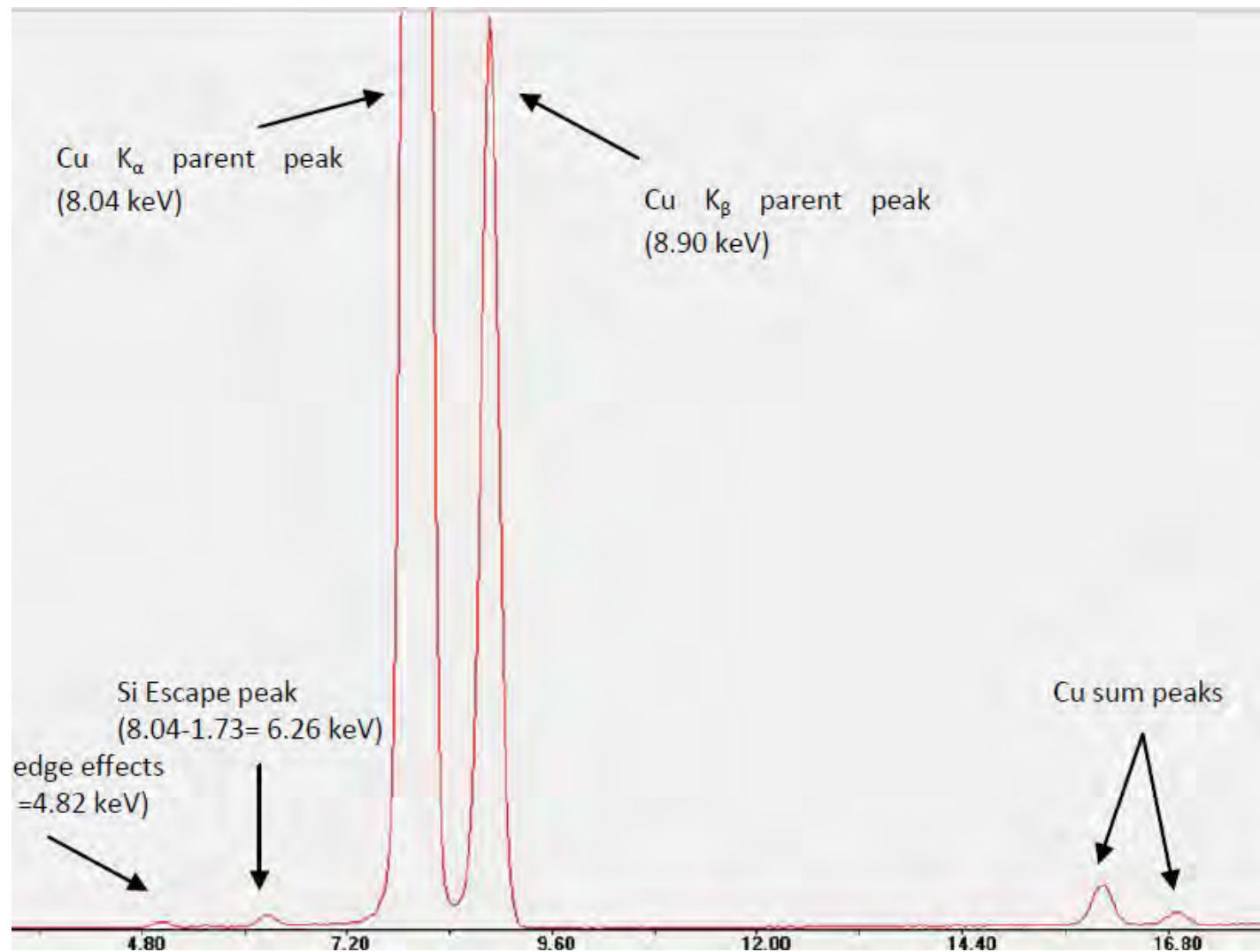
Escape Peaks

While most characteristic x-rays entering the detector are converted into pulses which are processed by the digital pulse processor, an incoming x-ray can excite and cause fluorescence in an atom in the detector. If the x-ray entering the detector has an energy greater than the absorption edge of an element in the detector (for the Tracer: Silicon), then fluorescence in the detector may occur. The inbound x-ray will lose the amount of energy required to fluoresce the detector atom, leaving the x ray with an energy $E' = E_{\text{inbound}} - E_{\text{Characteristic}}$, thus causing the detector to read the x ray as having an energy of E' .

Escape peaks are much less intense than the characteristic peaks from which they are derived. Several escape peaks can occur in one spectrum, given that all characteristic energies above the absorption edge of the detector are capable of causing fluorescence. In the case of a Si based detector, escape peaks will appear approximately 1.74 keV lower than a characteristic peak because silicon has a $K\alpha$ absorption edge.

Data Evaluation – Reading Spectra

Escape Peaks



Data Evaluation – Reading Spectra

Instrument Artifacts

As the incident radiation travels from the source to the sample, it may cause fluorescence in materials in the instrument which may be detected and shown on the spectrum. The target element may be detected, as well as iron, zinc, copper, and nickel in the tube, collimators, lens, etc.

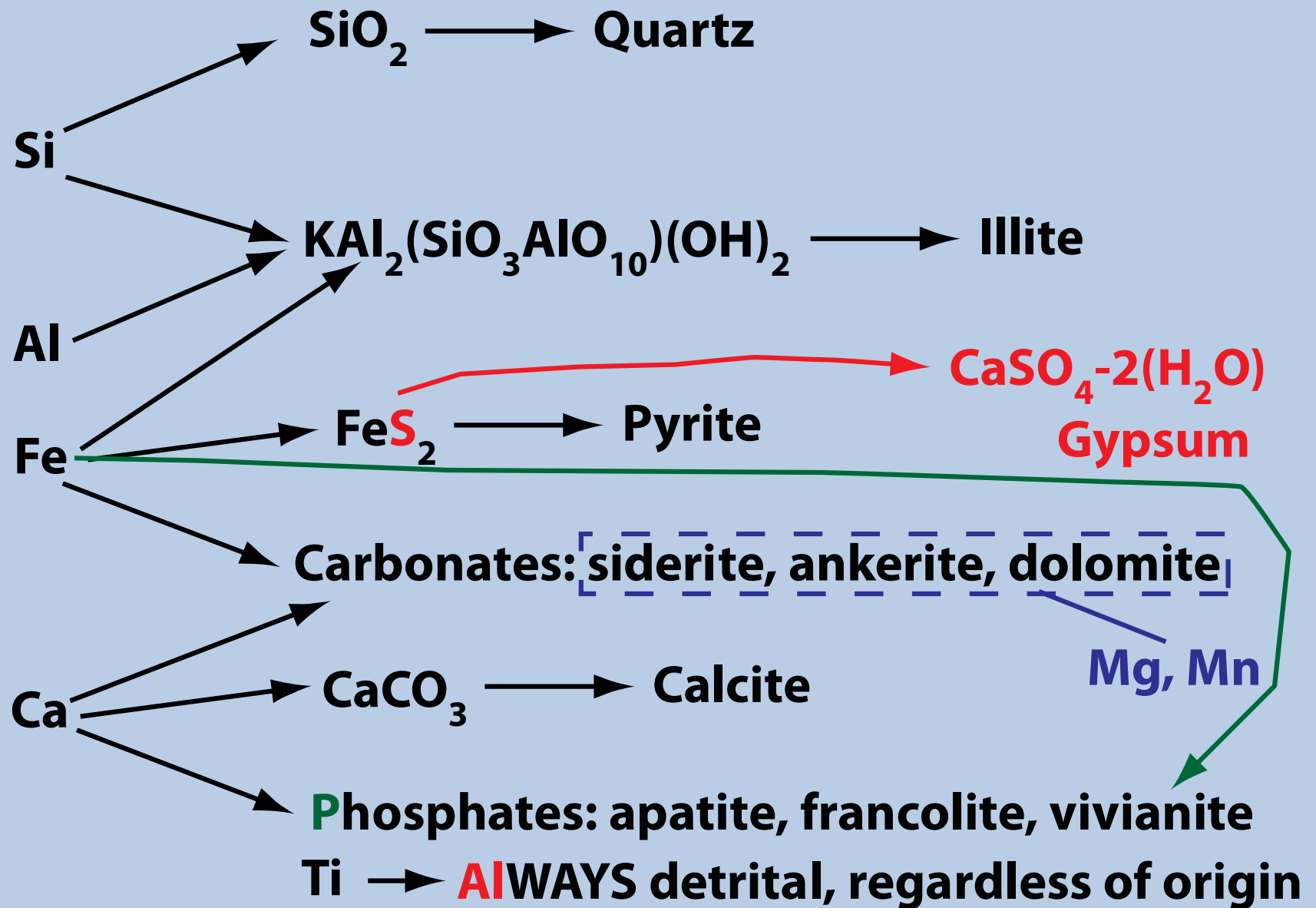
- X-ray tube target K and L lines (e.g. Rh)
- Stainless Steel Detector Can Lines (e.g. Fe, Co, Ni, only appear when testing low Z elements)
- Window lines (e.g. Ca)
- Collimator and instrument structure (e.g. Pd)
- If using a thin film sample, elements in surface below the sample

By adding a filter in between the tube and the sample, much of this unwanted radiation can be removed from the spectrum.

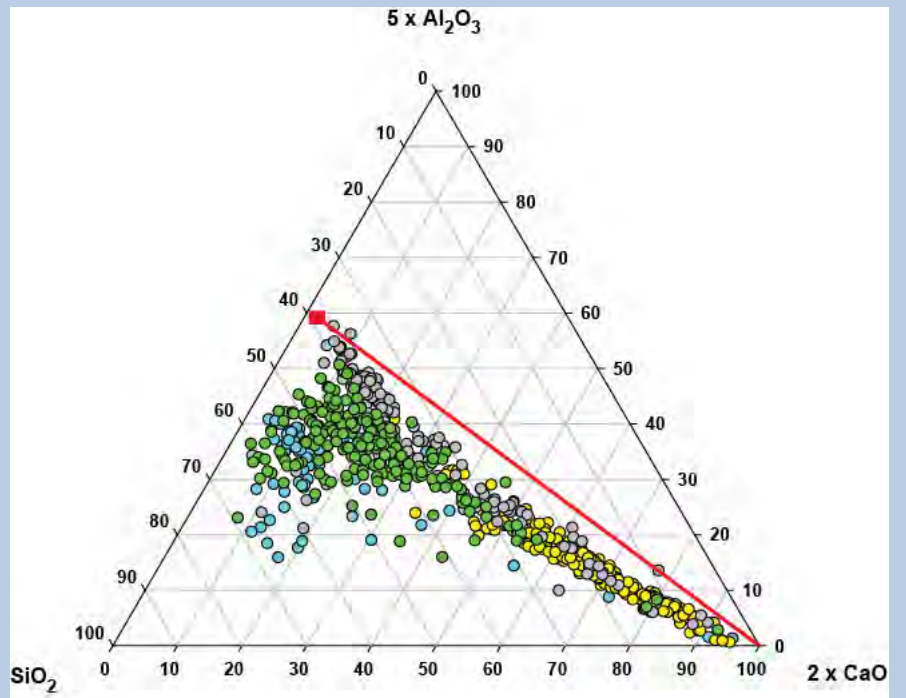
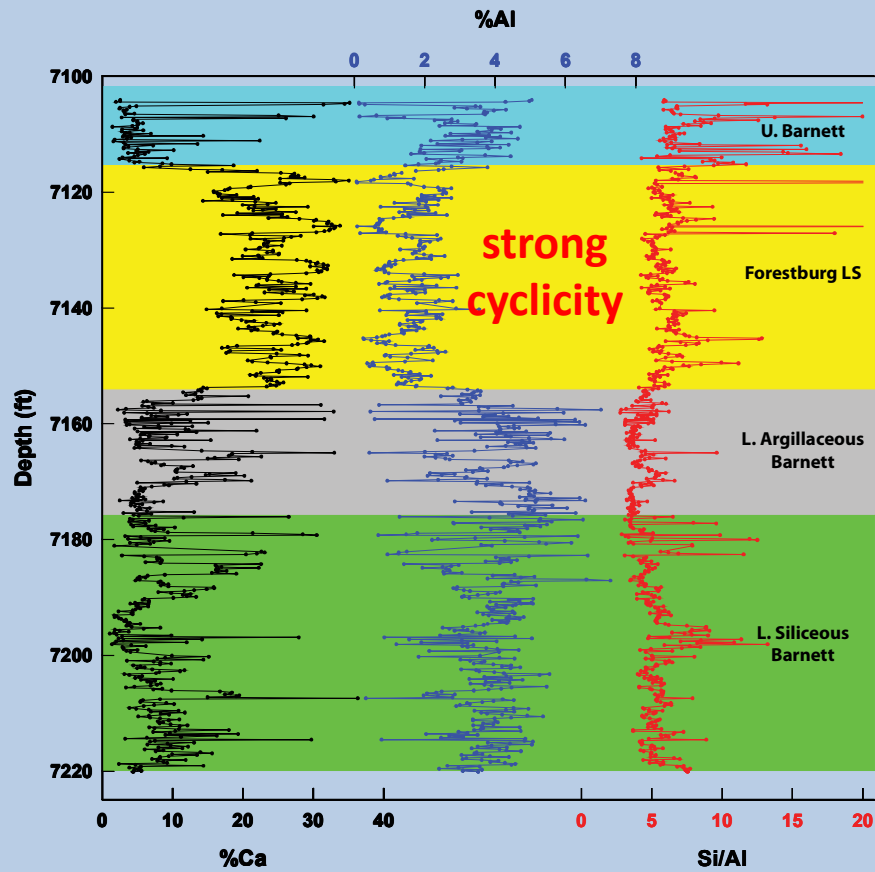
GEOCHEMICAL AND
CHEMOSTRATIGRAPHIC APPLICATIONS OF
XRF ANALYSIS

HARRY ROWE
BUREAU OF ECONOMIC GEOLOGY

Geochemical Model for Sample Mineralogy



Barnett Shale, SE Wise Co., TX

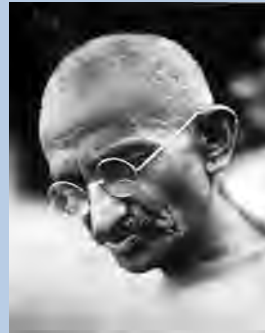


How can we think about these records?



- View these different lithologies as falling somewhere along a “*clay-carbonate continuum*”.....
- And, just as lithology/facies may reflect petrophysical characteristics, so shall the “chemofacies” ...which may be a more quantitative way of making the linkage between facies and petrophysics....it is certainly faster.
- At the very least, chemostratigraphy brings more evidence for/against ideas developed through facies identification/analysis.

Let's Think Deeper

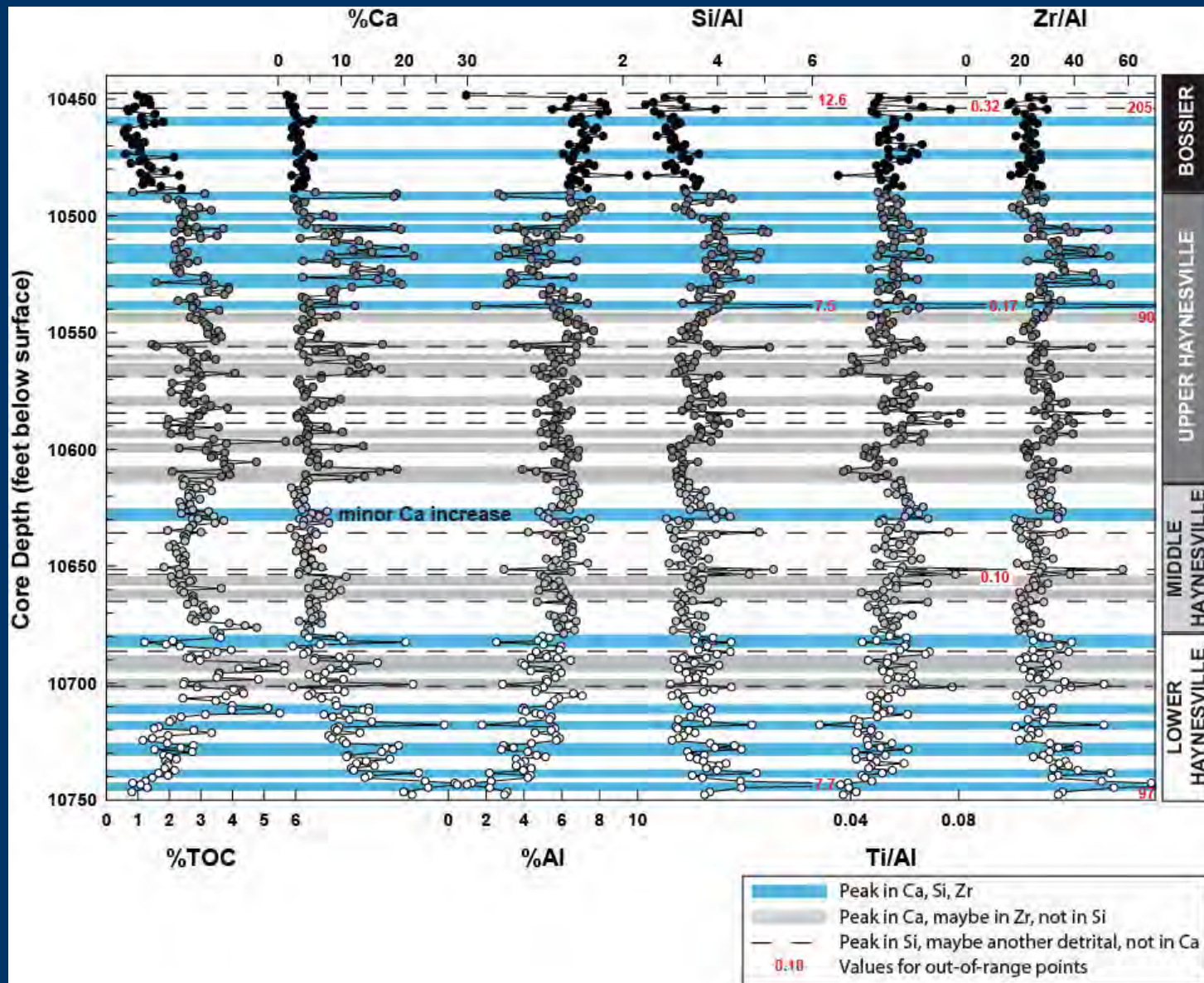


- **Problem #1:** In black (or any color) shales, we can't visually see much of anything....
- **Problem #2:** In carbonates, we can't see the small stuff (diluted by fossils, diluted by overabundance of Ca)

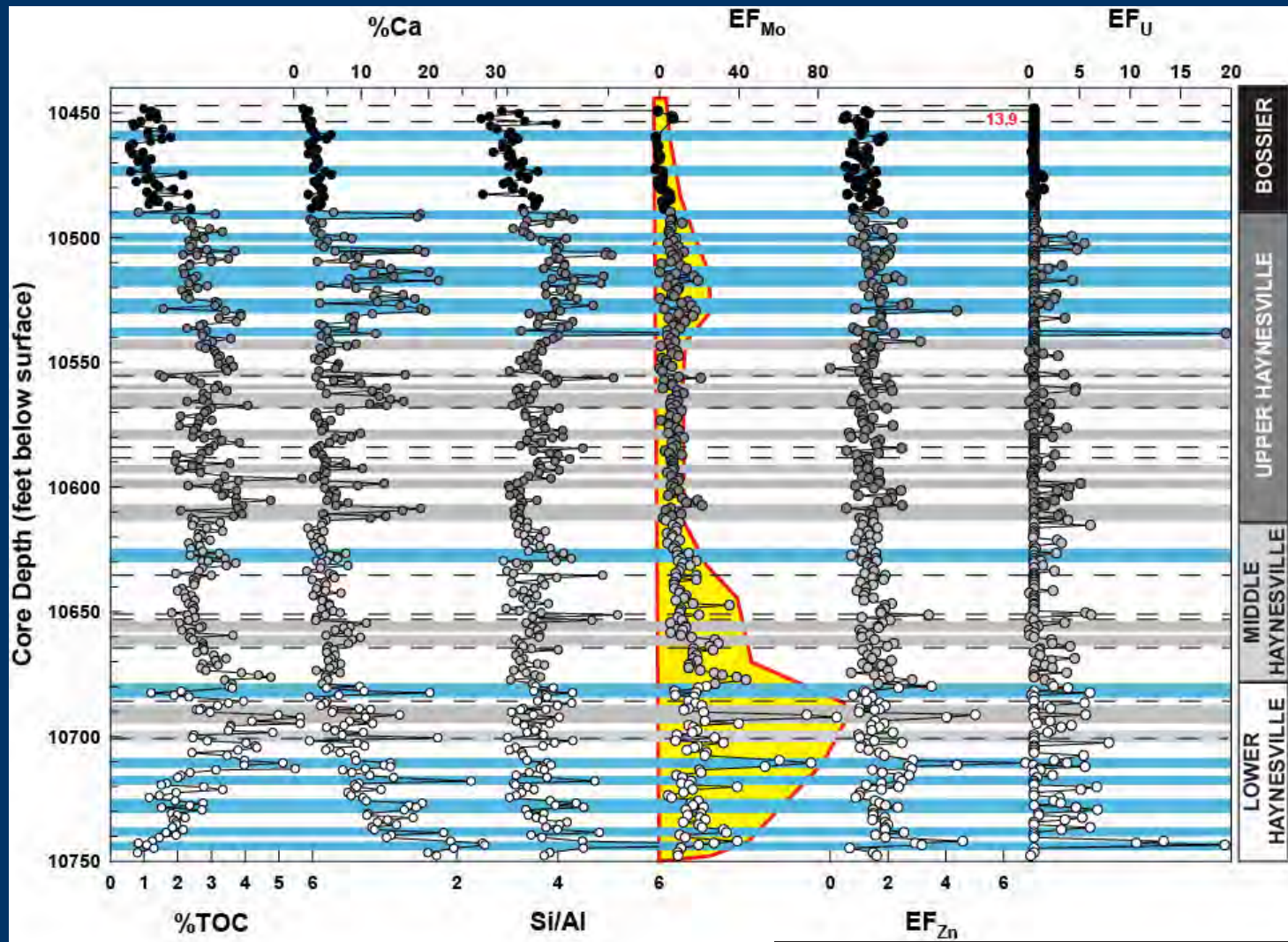
- Best thing might be to have mineralogy (XRD)—only if there are different minerals.
- **Problem#3:** a) Takes too long; b) Everybody does it slightly differently, leading to variable results; c) Biggest problem is quantifying clay content and type.
- **Problem #4:** While shales/mudrocks have diverse mineralogies, the mineralogy is overwhelmingly calcite/dolomite in carbonates...that's why they're called carbonates.

- **Solution:** Elemental geochemistry--specifically, a geochemical model that can infer and be *checked* with mineralogy (XRD).
- **Bonus:** Some elements can provide additional information---which might even be useful! Example: redox-sensitive trace elements (RSTEs).
- **Icing on the cake:** Not only can the model be *checked* with XRD, but elemental geochemistry can tell us where to take the limited XRD samples.

Chemostratigraphy: Carthage Core, Panola Co., TX

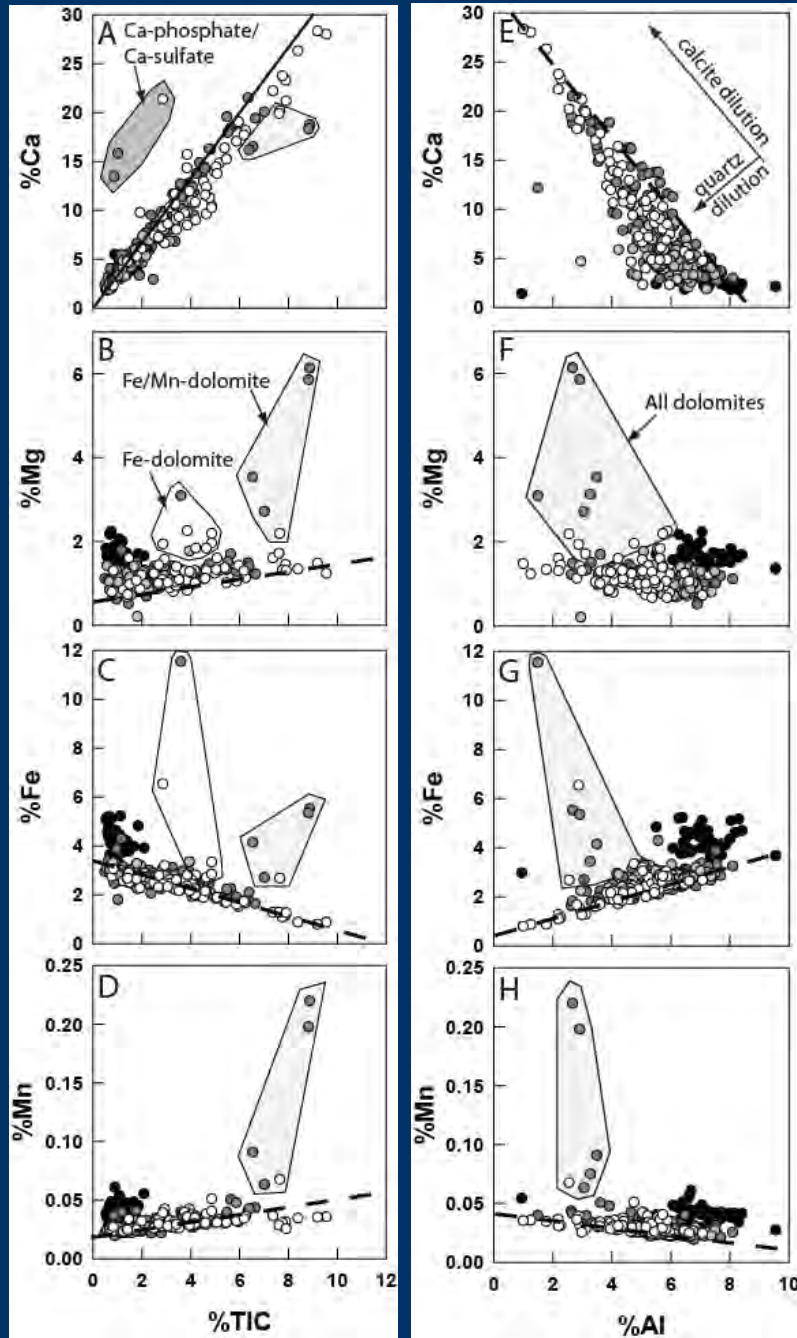


Chemostratigraphy: Carthage Core, Panola Co., TX



 Peak in Ca, Si, Zr
 Peak in Ca, maybe in Zr, not in Si
 Peak in Si, maybe another detrital, not in Ca
0.10 Values for out-of-range points

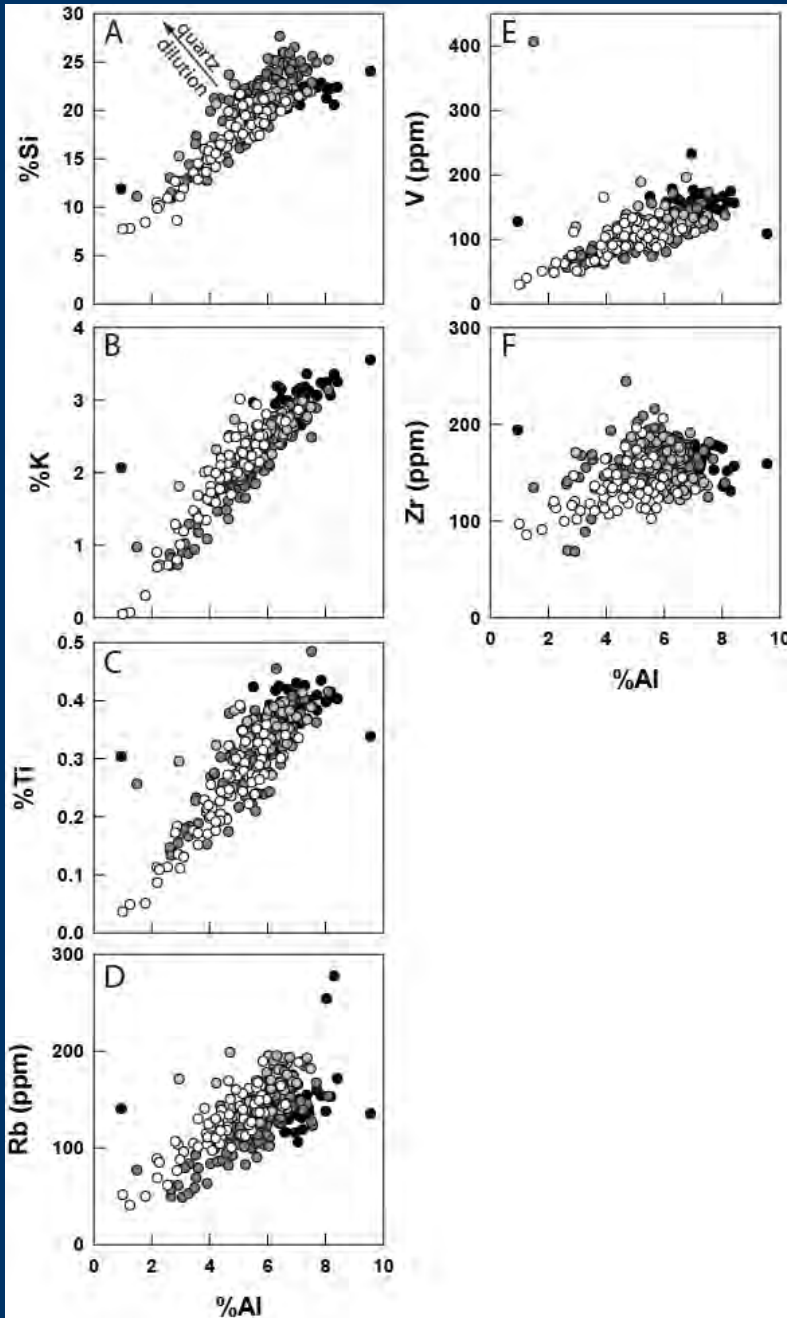
Elemental BiPlots: Carthage Core, Panola Co., TX



- **Ferroan and manganoan dolomite/ankerite**
- **Mild manganoan calcite**
- **Most Fe is in clays**

● Bossier
 ● Upper Haynesville
 ○ Middle Haynesville
 ○ Lower Haynesville

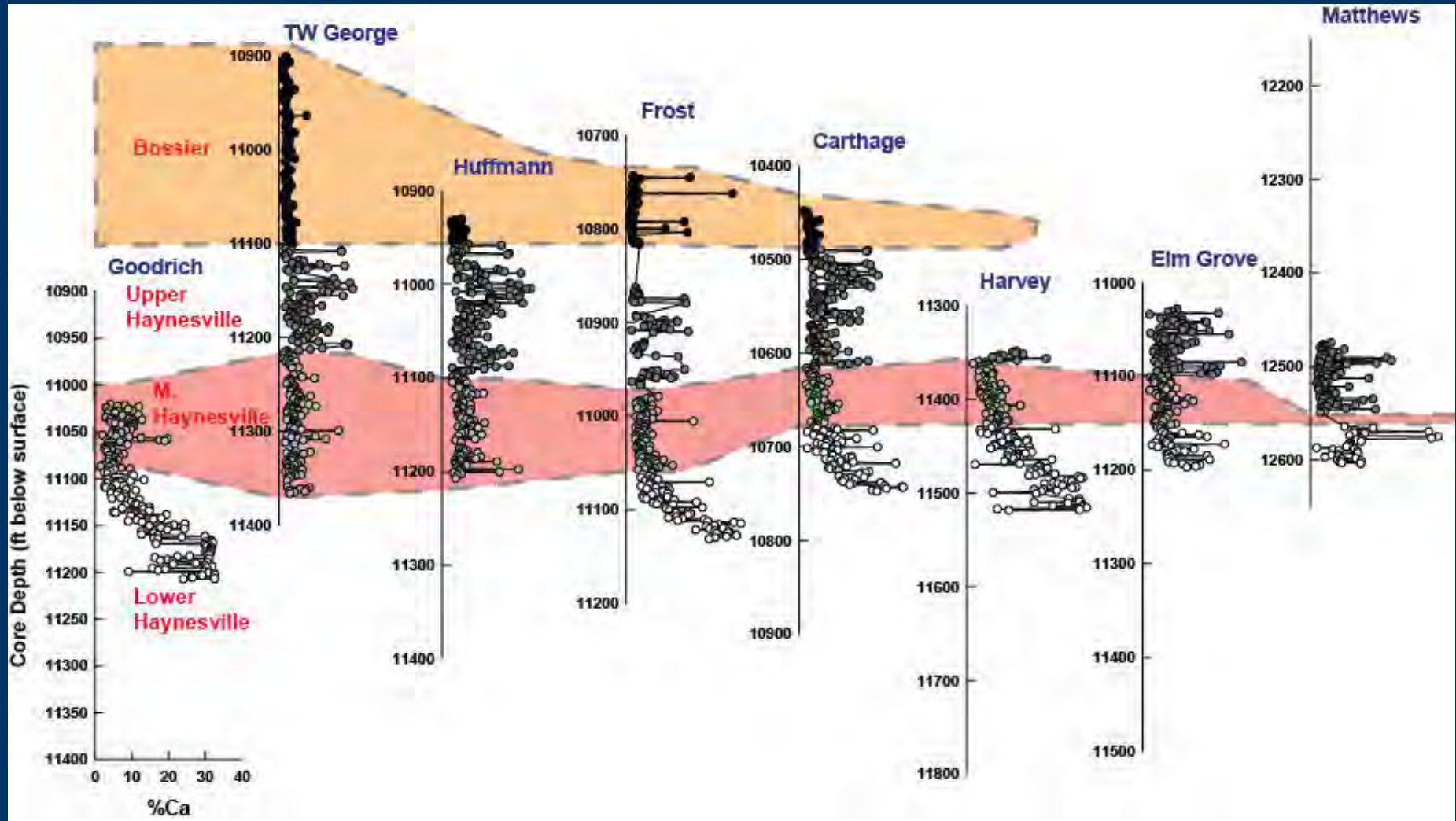
Elemental BiPlots: Carthage Core, Panola Co., TX



- **Si-Al line demonstrates clay with quartz**
- **K and Ti can be used as detrital (clay) proxies**
- **V—mostly of detrital origin!!**
- **Zr and Al are not strongly linked, suggesting difference in transport or origin (grain size)**

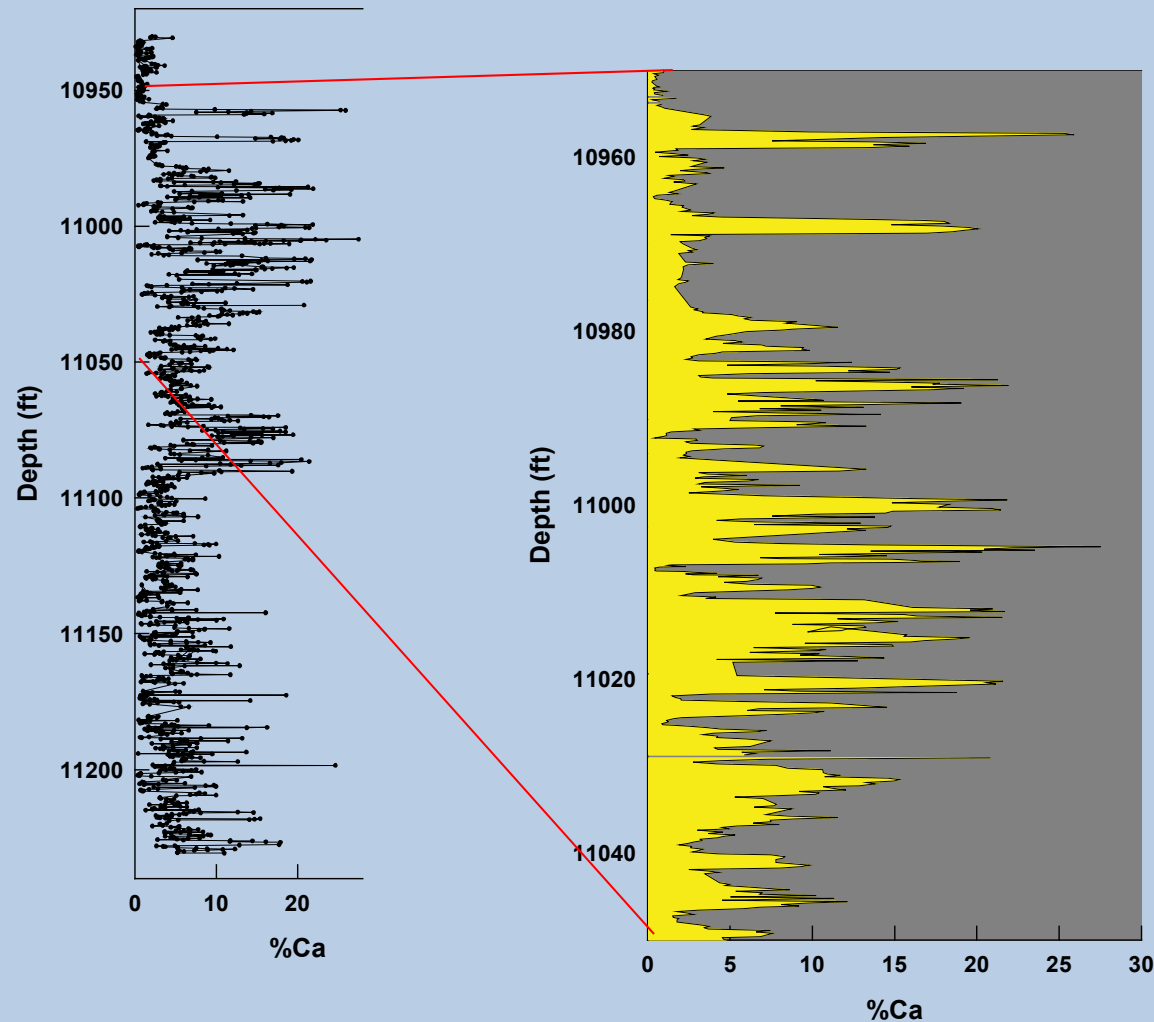
● Bossier
● Upper Haynesville
○ Middle Haynesville
○ Lower Haynesville

Chemostratigraphic Correlation: %Ca



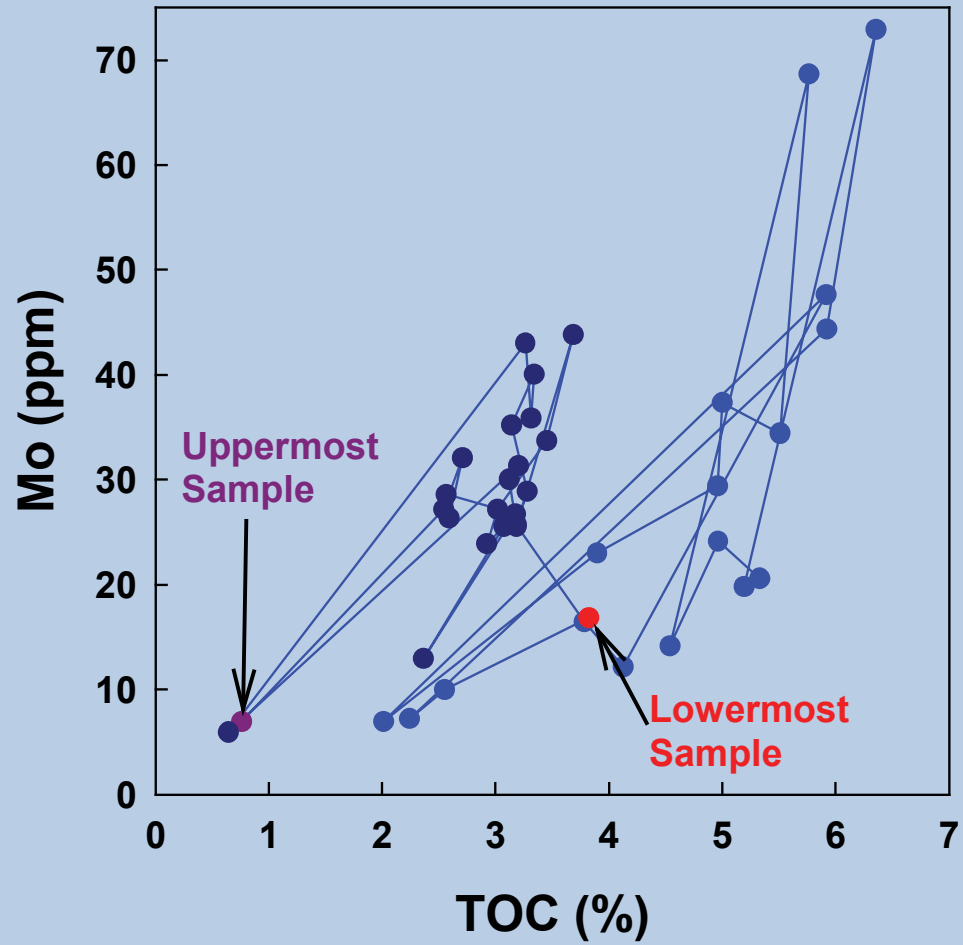
- %Ca is high and upwardly descending in the Lower Haynesville chemofacies.
- %Ca is low and largely invariant in Middle Haynesville chemofacies.
- %Ca has an expanded range and is "jumpy" in the Upper Haynesville chemofacies.

Haynesville Closer Look (Huffman Core, Panola, Co., TX)

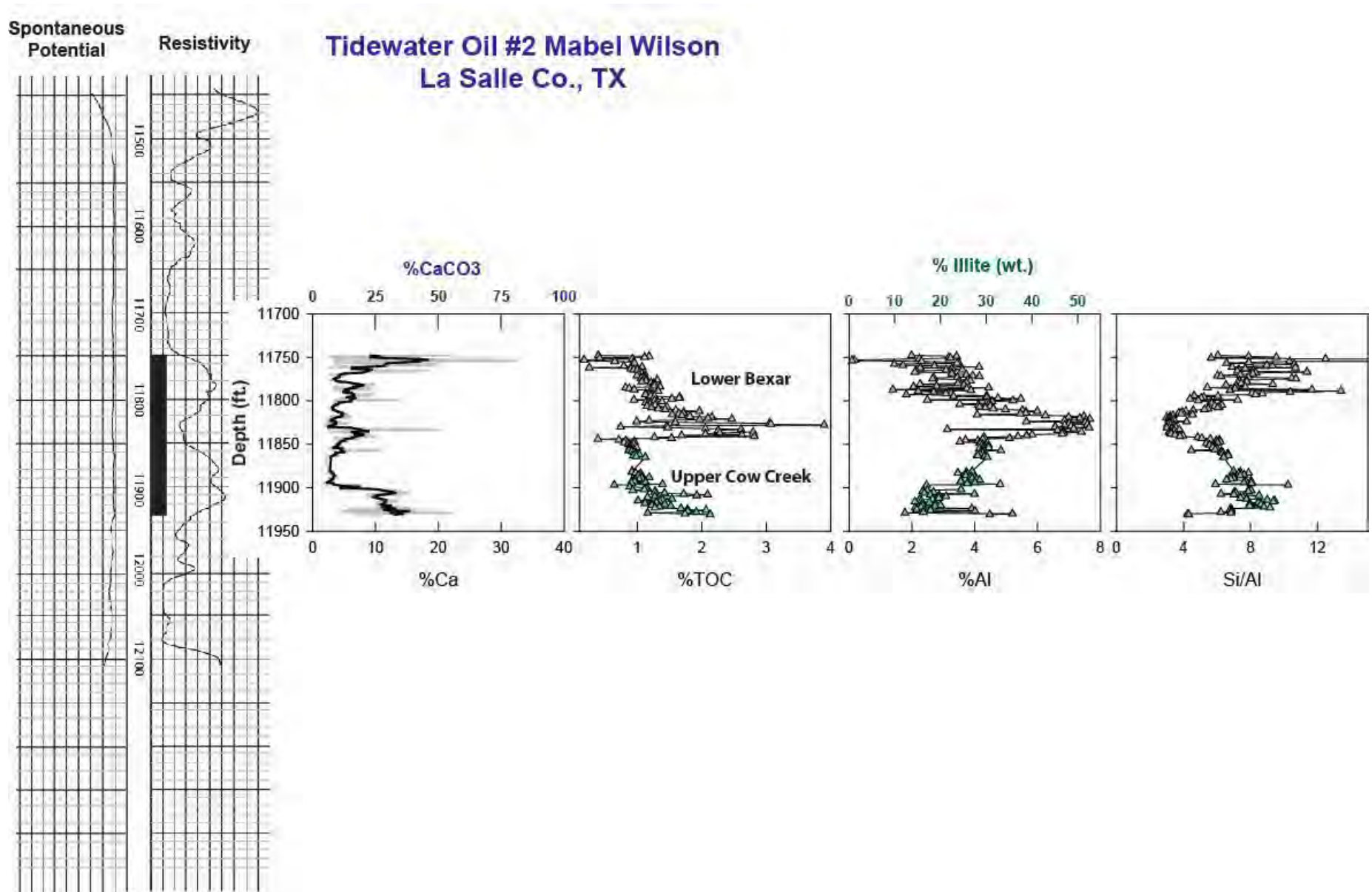


- Cause of cyclicality (cyclicities!)?
- Significance for depositional environment interpretations?
- Significance for understanding highly oscillatory inter-bed competency and building the petrophysical model.

Mo-TOC Relationship in the Hay Core



Integration of Logs and Chemostratigraphy



Integration of Logs and Chemostratigraphy

