Analytical Methods for the Study of Trace Elements in Geologic Materials

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Types of Geologic Samples

- Rocks
- Soil
- Stream sediments
- Water
- Air borne dust

SAMPLE COLLECTION

- **Coal**
  - -Cores
  - -Channels
  - -Grab
  - -Continuous samplers
  - -Power plant feed
  - -Washed
  - -Fines, coarse, midlings, rejects
  - -Fly ash, bottom ash, FGD
  - -Etc.

Sample Handling

- Prevent oxidation
- Minimize moisture loss
- **Avoid Contamination**

Analytical Methods for Characterizing Geologic Materials

Chemical Analysis

***Bulk Sample**

-Inductively coupled Plasma (ICP) AES & MS

-Instrumental neutron Activation analysis (INAA)

-X-ray fluorescence (XRF)

-Atomic Absorption Spectroscopy (AAS)

***Micobeam**

-Electron microprobe

-Scanning electron microscope

-Ion microprobe

-Laser mass analyzer

Summary of Some of the Characteristics of the Trace Element Analysis Techniques

Technique	Instrument Price[a]	Detection Limits[b]	Spectral Interference	Matrix Effects	Multi-elemental	Sample Type
INAA	+++	0.001-1	low	low	yes	solid
ED-XRF	+	1-10	high	medium	yes	solid
WD-XRF	++	0.1-1	low	medium	yes	solid
PIXE	+++	1-10	high	medium	yes	solid
ICP-AES	+ to ++	1-30	high	medium	yes	liquid
ETA-AAS	+	0.01-0.2	medium	high	no	liquid
ICP-MS	++ to +++	0.03-0.1	high	high	yes	liquid

[a] + less than $100,000 to $250,000; +++ more than $250,000.

[b] μg/g for solid sample type; ng/ml for liquid sample type

Detection Limits (in μg/g solid sample)						
Element	INAA	ED-XRF[a]	PIXE[a]	ICP-AES[b]	ETA-AAS[b]	ICP-MS[b]
V	0.03	20	1.3	3.5	0.2	0.03
Cr	0.03	16	0.8	4	0.01	0.06
Mn	0.001	12	0.6	0.95	0.01	0.10
Fe	6	12	0.5	3	0.02	
Ni	3	5	0.4	6.5	0.2	0.10
Cu	0.03	6	0.3	3.5	0.02	0.32
Zn	0.3	5	0.3	1.2	0.001	0.21
As	0.03	4	0.4	35	0.2	0.04
Se	0.03	2	0.4	50	0.5	0.79
Mo	0.3	5	1.9	5.5	0.02	0.04
Cd	0.6	6	10	1.7	0.003	0.06
Sn	1	8	16	17	0.1	0.06
Sb	0.01	8	14	20	0.1	0.05
Hg	0.003	7	1.0	17	2	0.02
Pb		8	1.1	30	0.05	0.05

From W. Maenhaut, *Nucl. Instr. and Methods B49,* 518 (1990).

[a] For 1 mg/cm^2 samples of a light element matrix.

[b] For solutions containing 0.1% dissolved solid sample.

Methods for Determining Trace Elements in Coal and Coal By-Products

Element	INAA	XRF[a]	ICP-AES	AAS[b]	ICP-MS	CHEM
Be	--	--	X	X	X	X
B	--	--	X	--	X	X
F	--	--	--	--	--	X
Cl	X	X	--	--	--	X
V	X	O	X	X	X	
Cr	X	X	X	X	X	
Co	X	X	X	X	X	
Ni	X	X	X	X	X	
Cu	O	X	X	X	X	
Zn	X	X	X	X	X	
As	X	X	O	X	X	
Se	X	O	X	X	X	
Mo	X	X	X	X	X	
Cd	--	O	O	X	X	
Sb	X	O	X	X	X	
Ba	X	X	X	X	X	
Hg	O	O	O	X	X	
Pb	--	X	X	X	X	

X-generally suitable

O-limited by sensitivity or interference

-- -generally unsuitable

[a] Includes ED-XRF, WD-XRF, or PIXE

[b] Includes F-AAS, ETA-AAS, or CV-AAS

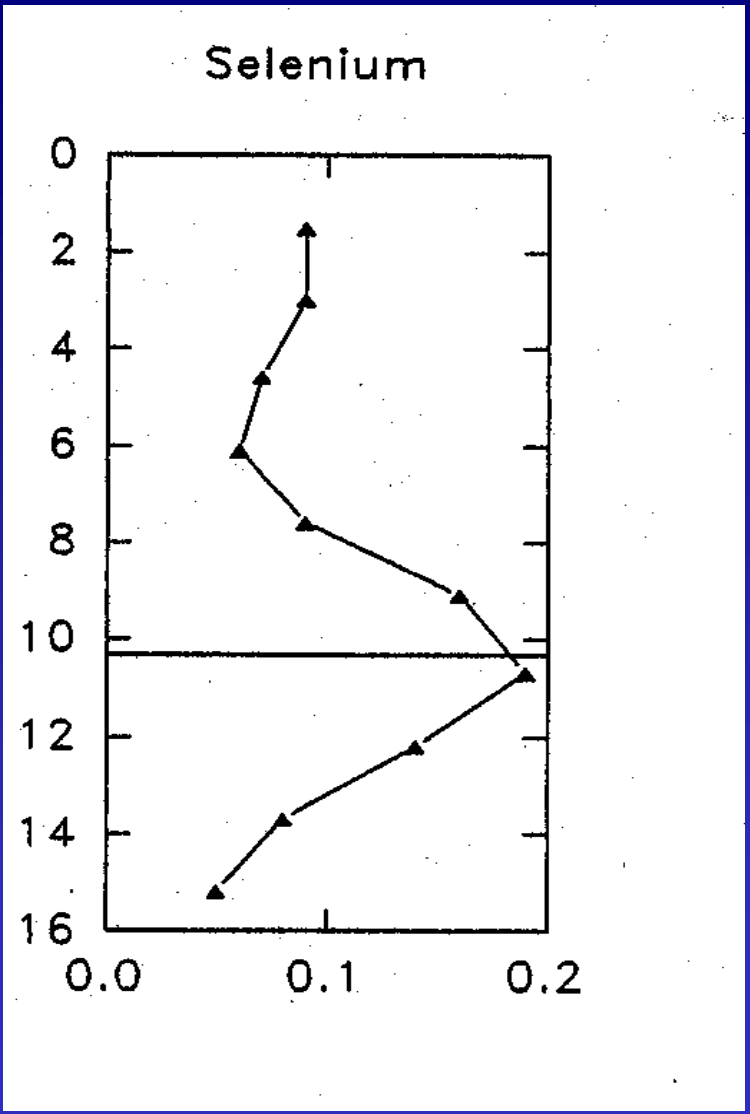
Speciation/ Modes of Occurrence

- Mineralogical characterization
- Microbeam analysis
- Wet chemistry
- Extended X-ray analysis fine structure (XAFS)

MODES OF OCCURRENCE

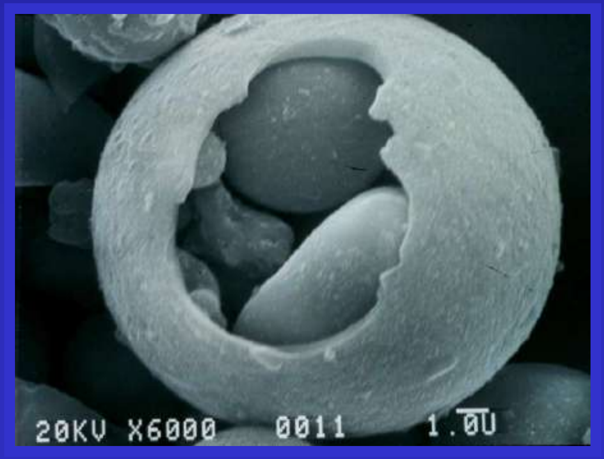
- Chemical form of the element
- Influences behavior during cleaning, combustion, conversion, leaching, weathering, etc.
- Determines environmental impact, technological behavior, by-product potential
- Examples:
  - Calcium-Calcite, organic salt, clay, sulfate, feldspar, phosphate, etc.
  - Zinc-Sulfide (sphalerite ZnS)

Selenium in sediment profile



Scanning Electron Microscope

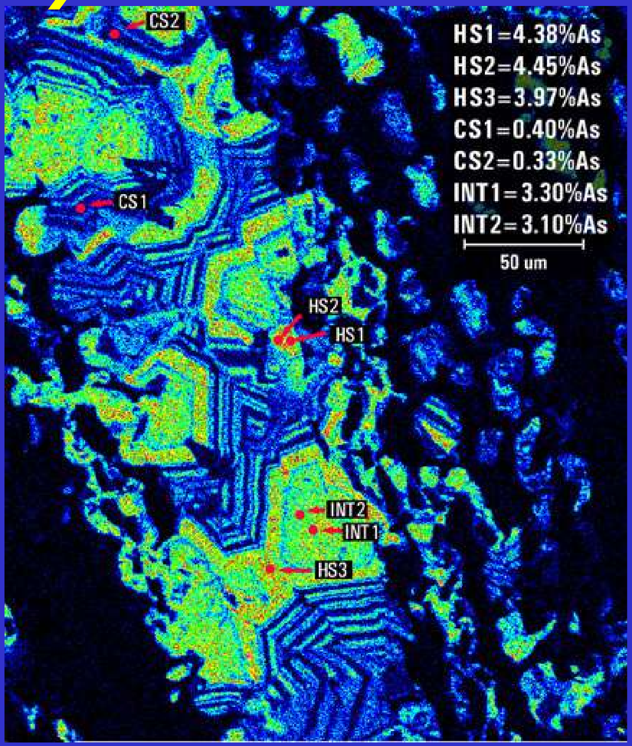
SEM Image of Fly Ash Particle



Electron Microprobe

Arsenic in Coal: Microanalysis

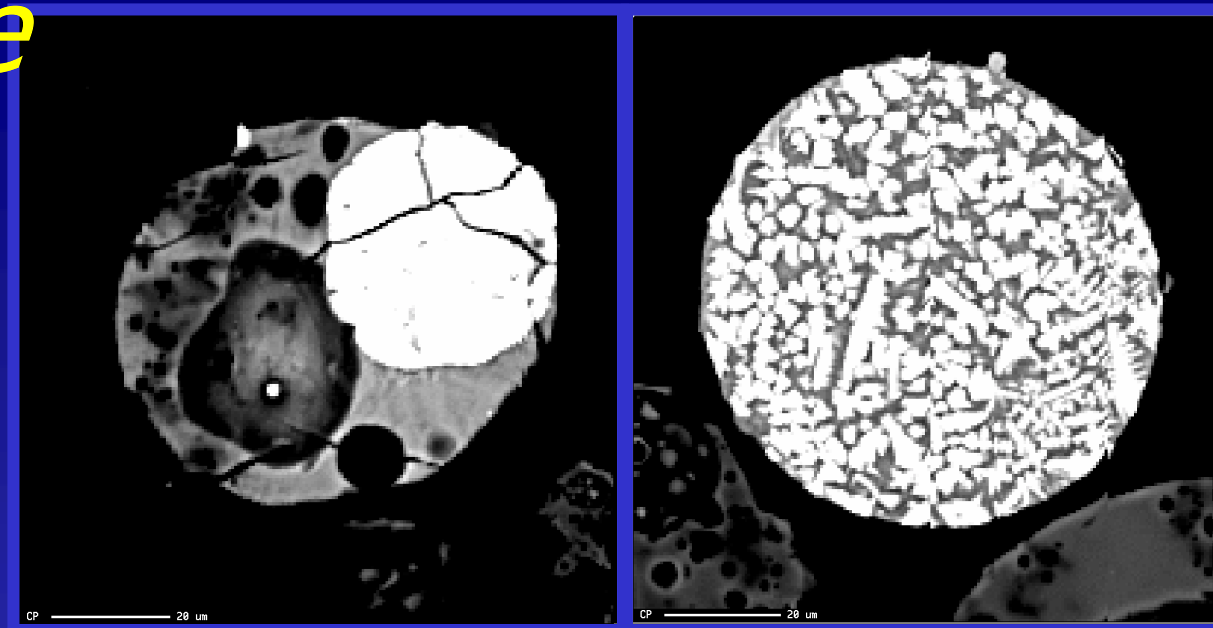
- *Arsenic is a trace to minor element in pyrite; concentrations ≥150 ppm can be determined using the electron microprobe.*
- *Direct confirmation of As residence indicated by other methods, but shows concentrations vary widely within and between grains.*



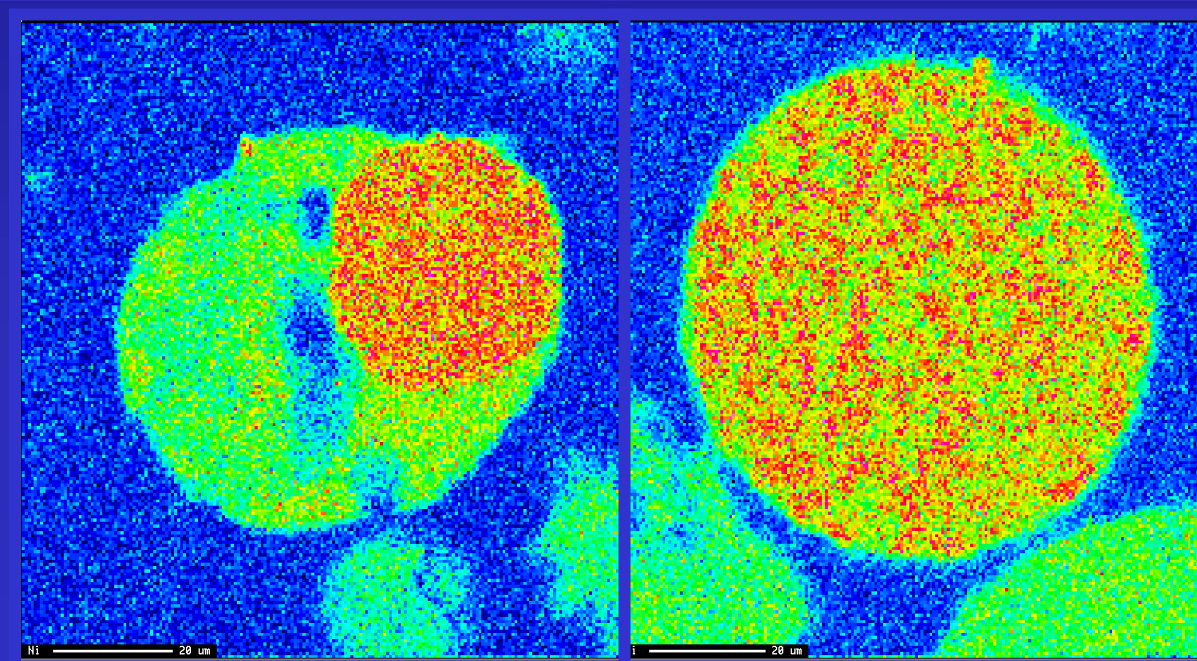
Arsenic-rich pyrite (to 4.5 wt. % As) with oscillatory zoning, Warrior Basin coal, Alabama.

Microprobe Results

Back-scattered Electron Images



Nickel Elemental Maps



SHRIMP-RG Ion Microprobe

Sensitive High-Resolution Ion Microprobe Reverse Geometry

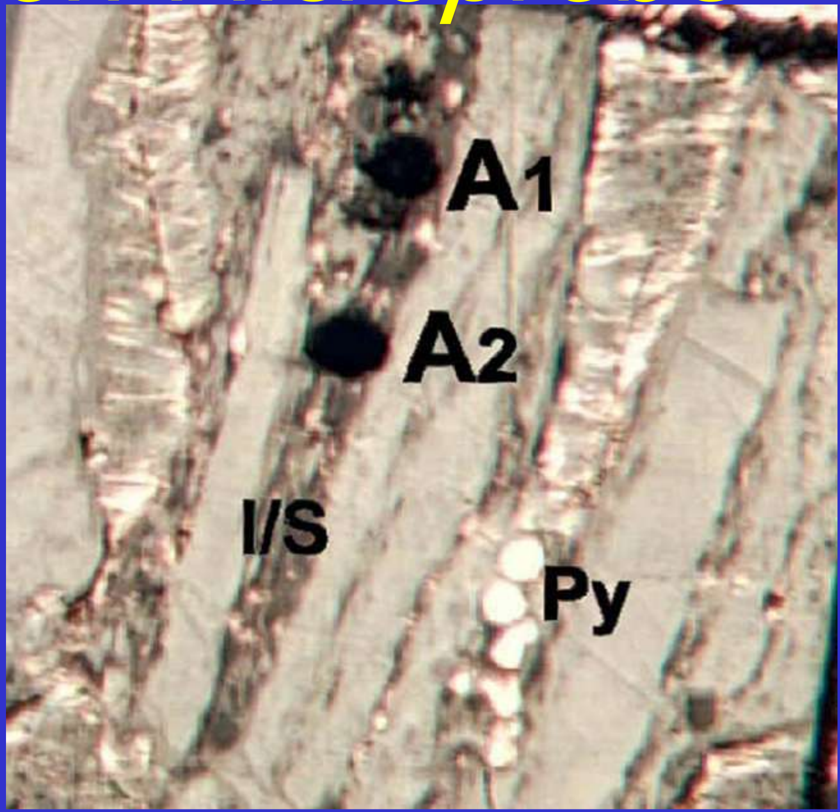
- Primary beam of O_2^- or Cs^+ ions
- Detection in the ppm range
- 10-15 micron spot size
- determine isotope ratios

Cr in Illite/Smectite in Coal: SHRIMP-RG Ion Microprobe

- *Quantitative results for silicate-hosted Cr using Stanford-USGS SHRIMP-RG ion microprobe.*
- *Concentration ranges:*

  Cr = 11 to 176 ppm
  Mn = 2 to 149 ppm
  V = 23 to 248 ppm

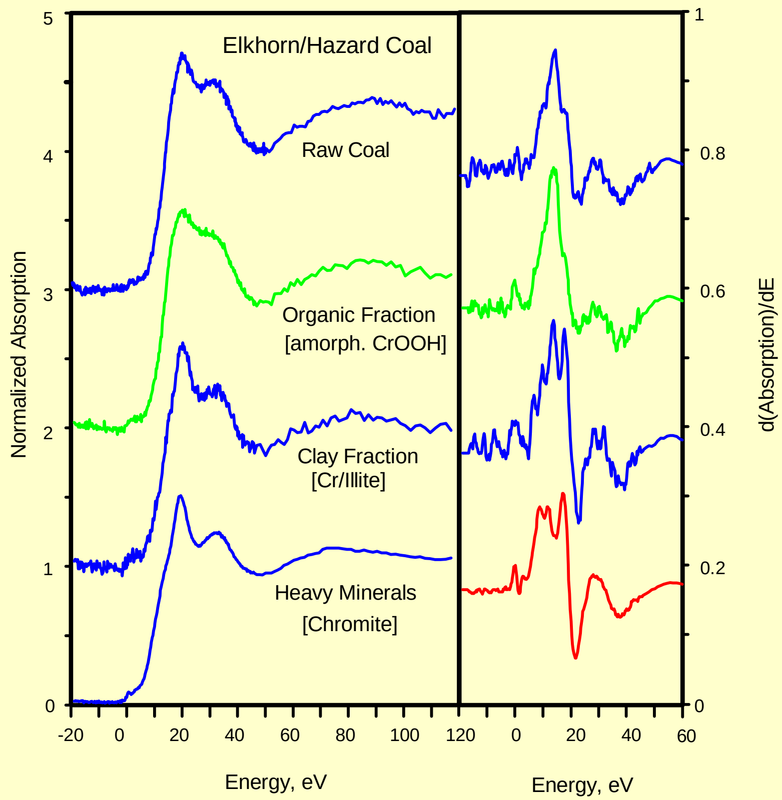
- *Confirms leaching results and electron microprobe data.*



Reflected-light image of illite band and SHRIMP-RG analysis points.

Chromium in Coal: XAFS

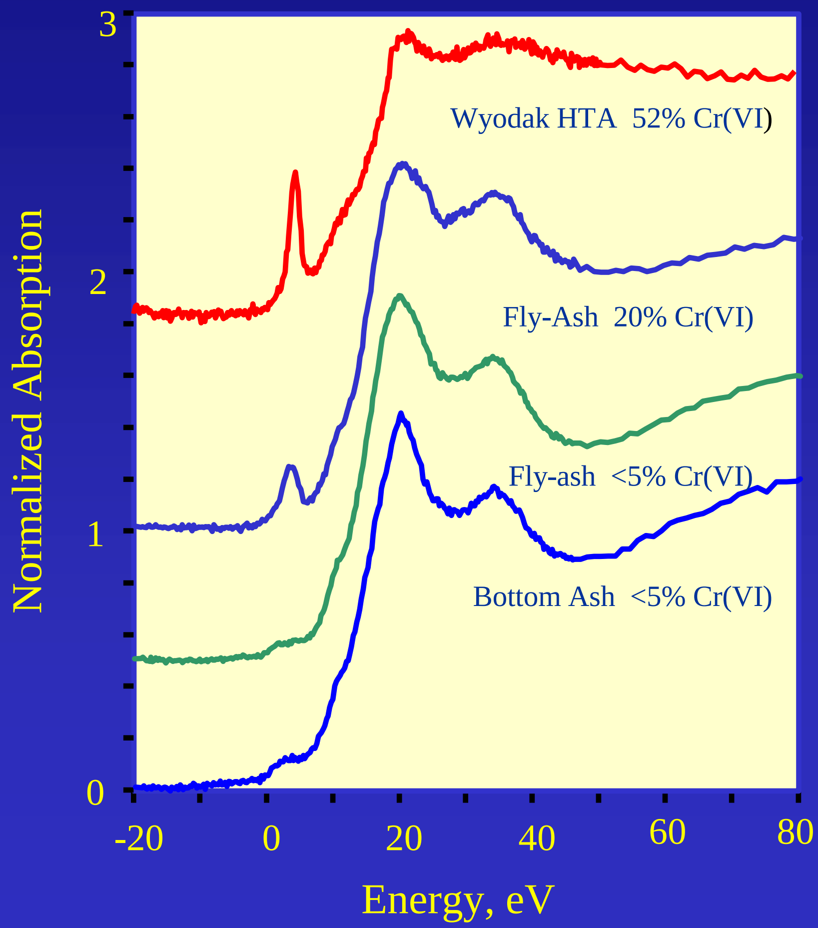
- *Two major forms identified:*
  - *Cr^{3+}/illite*
  - *Org. associated Cr (Amorph. CrOOH)*
- *Chromite- Common only in coals unusually rich in Cr*
- *Oxidation State- Always Cr^{3+}*



Chromium XANES spectra and derivatives for Elkhorn/Hazard coal and separated fractions. Note that a different spectrum is obtained for each fraction indicating that a different form of chromium dominates each fraction.

Cr in Ash: XAFS

- Cr can be found as:
  - Cr/spinel associated with magnetic iron oxides.
  - Cr associated with alumino-silicate glass.
- Oxidation State of Cr
  - Often <5% Cr as Cr(VI) in bottom ash and fly-ash from bituminous coals.
  - Rarely up to 20% Cr as Cr(VI) in fly-ash from lower-rank coals.

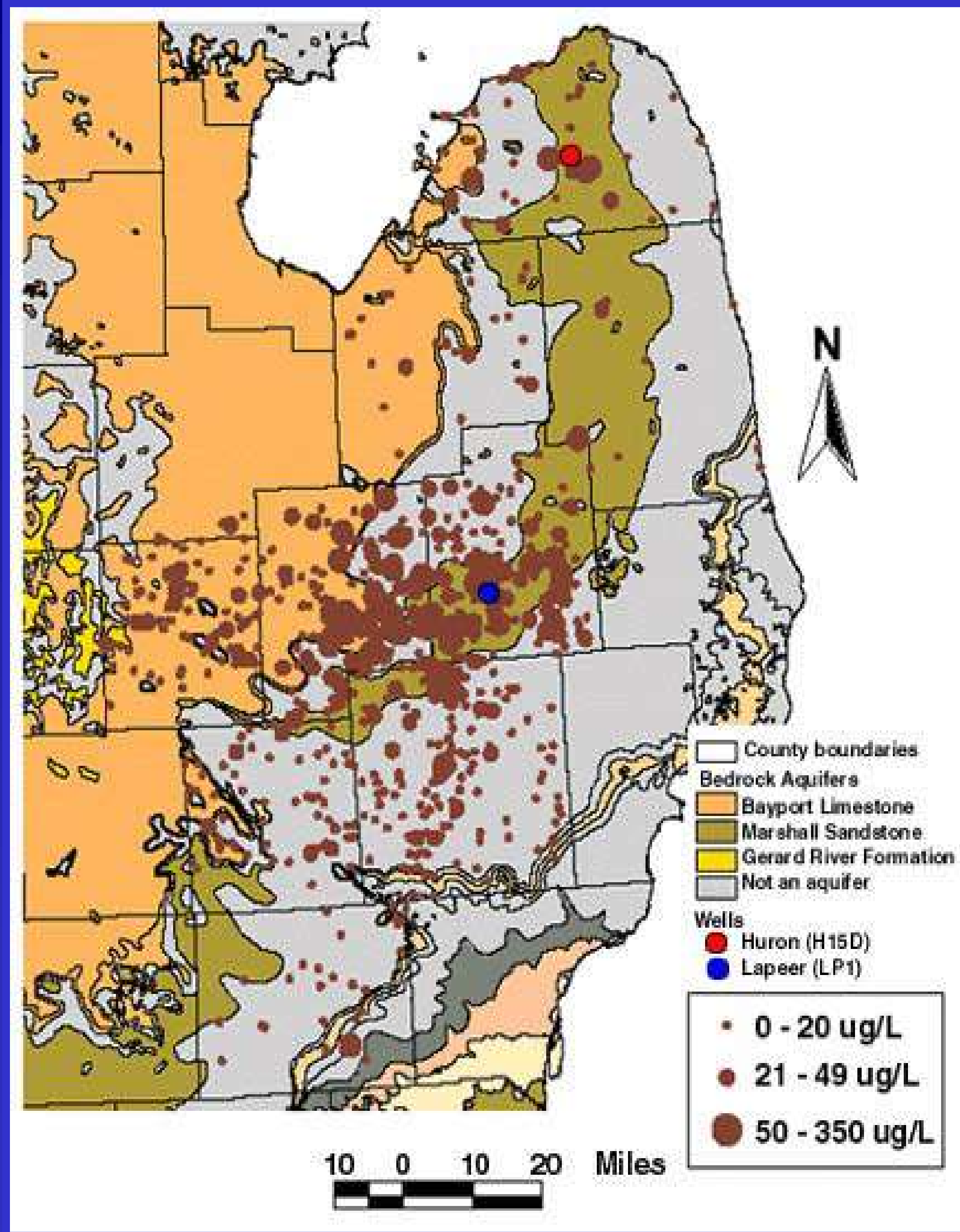


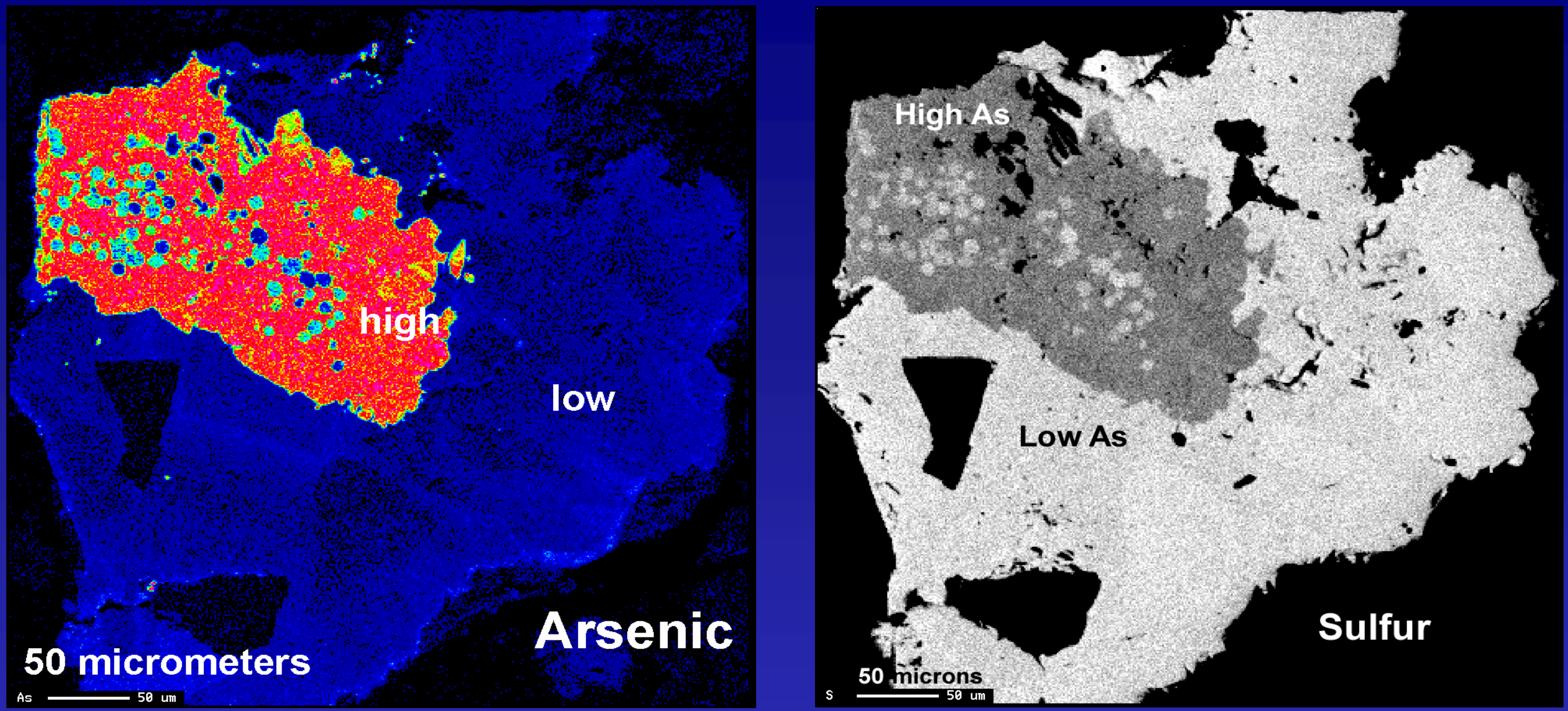
*Distribution of As-levels**

Max. arsenic is 6-8 times EPA standard.

Most problem wells are in the Marshall, but not exclusively so.

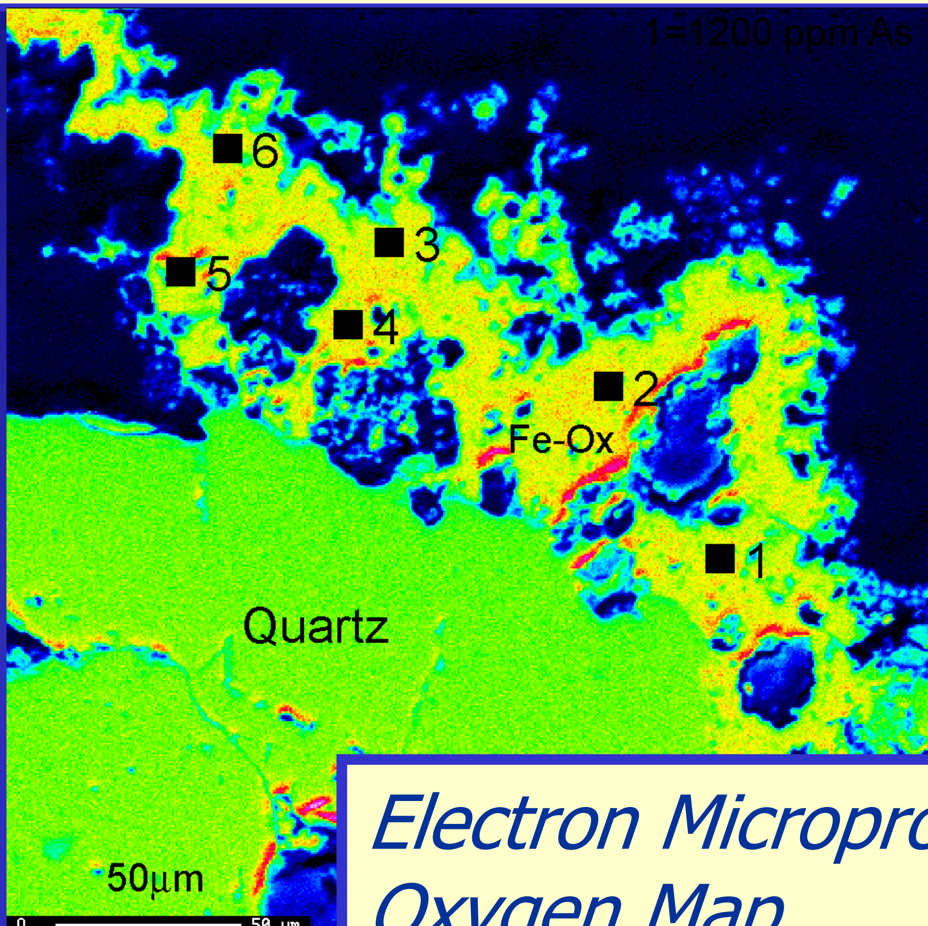
**MDCH data*





Electron microprobe elemental maps for As and S show high-As (6-7 wt. %) pyrite occurs as the second of 3 pyrite generations.

Arsenic-rich iron oxy-hydroxides (derived from pyrite) in till containing Marshall Sandstone



Electron Microprobe Oxygen Map

Arsenic (ppm)

1 = 1,200

2 = 1,300

3 = 3,300

4 = 1,400

5 = 2,800

6 = 1,000

Max. = 7,300

Conclusions

- *Microanalysis reveals the fine scale distribution of trace metals in coal and other geologic materials.*
- *This information is needed to predict the distribution and behavior of these metals in the environment, and to understand the source of metals that impact human health.*

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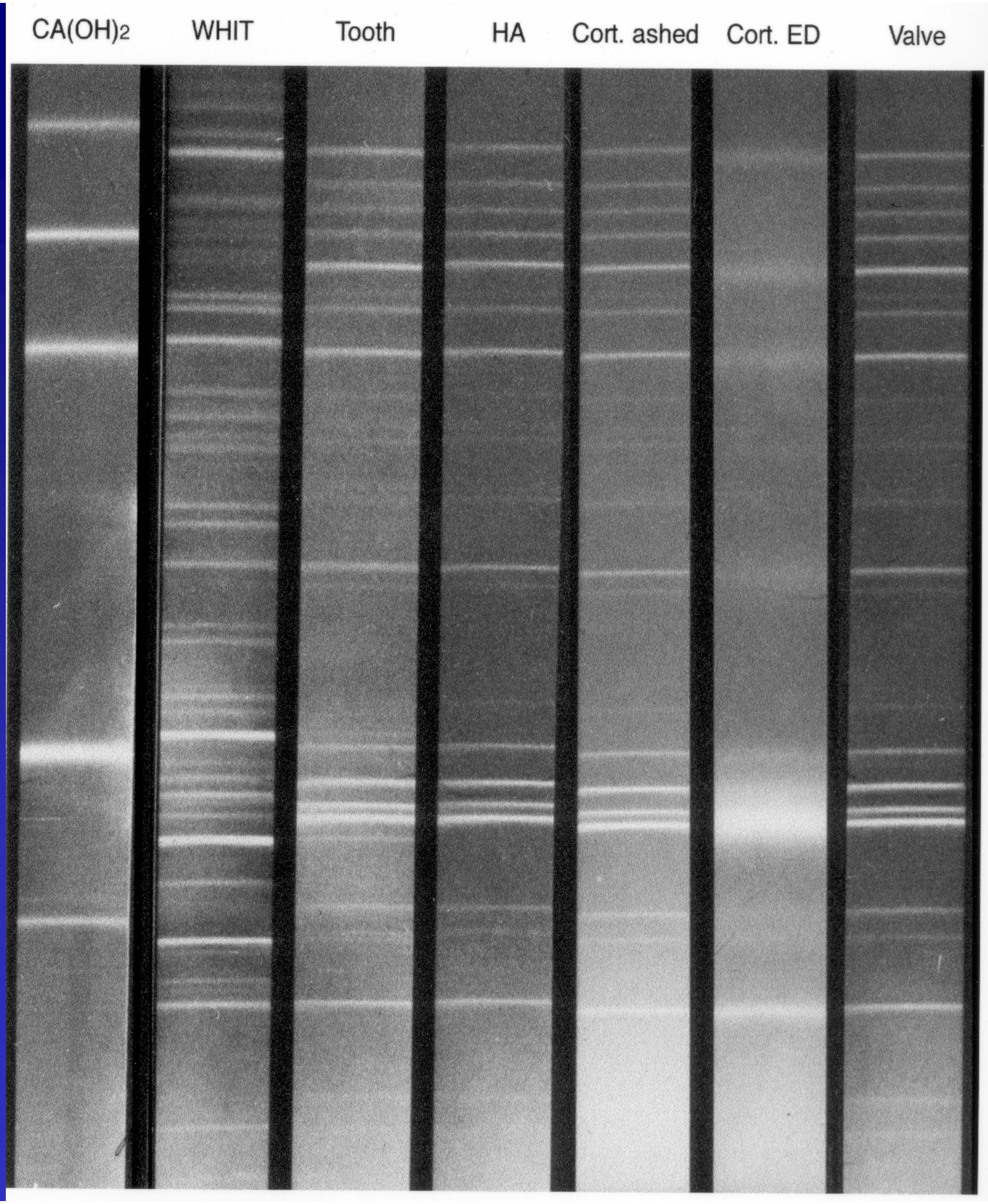
science for a changing world

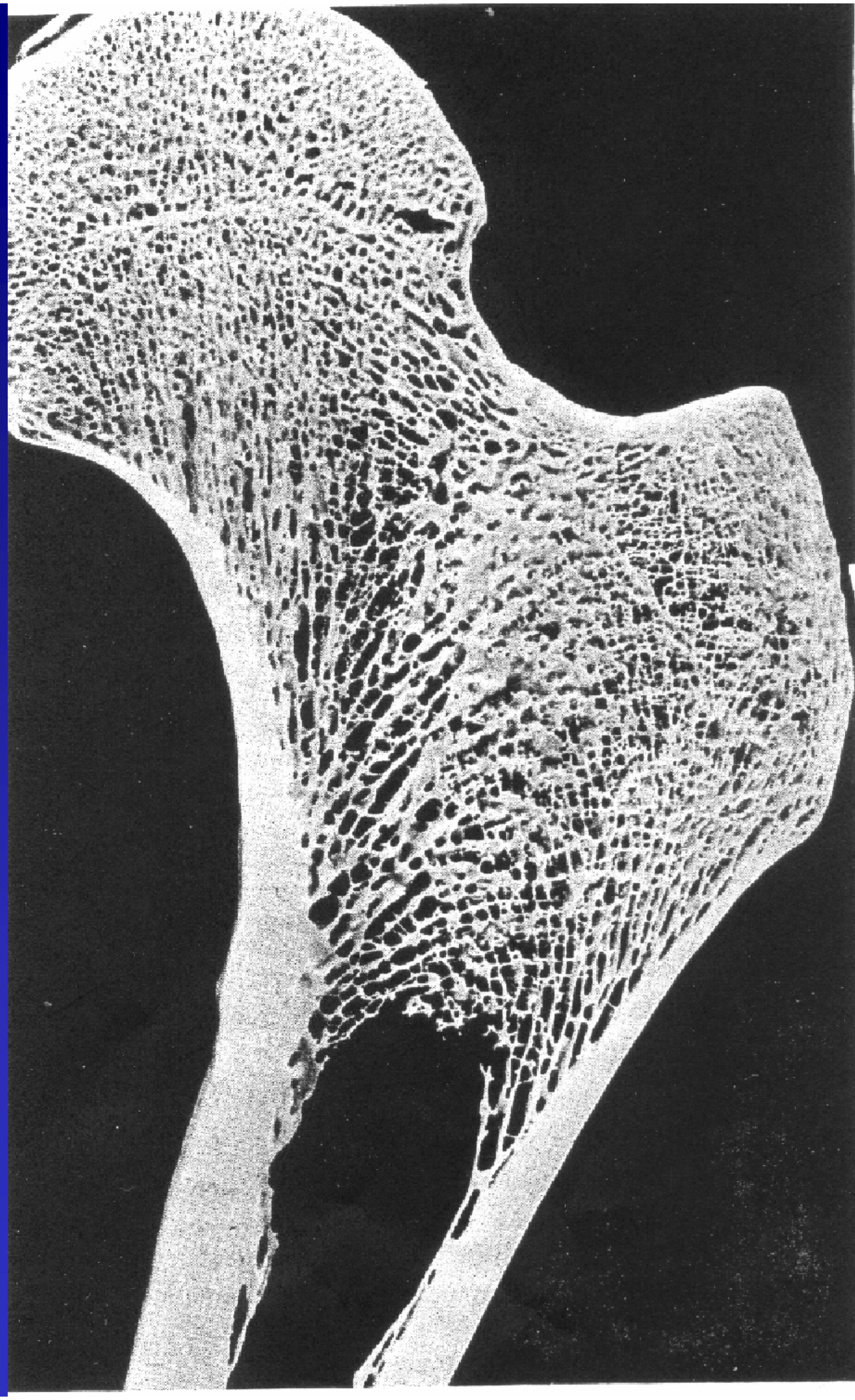
ANALYTICAL TECHNIQUES
FOR MINERALOGICAL CHARACTERIZATION

X-Ray Diffraction (Semi-quant./Direct)

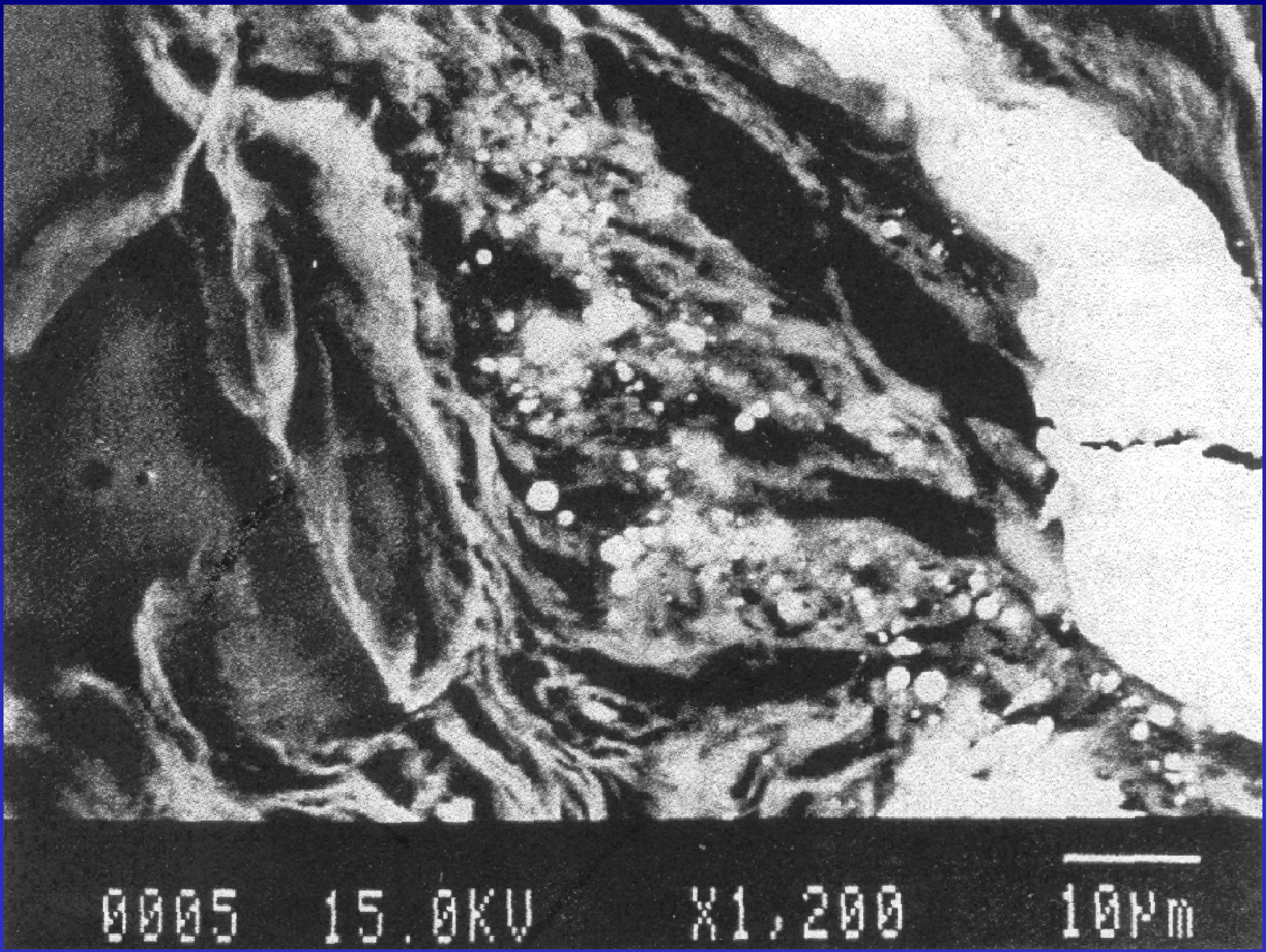
Scanning Electron Microscopy (Qual.-Semi-quant)
+Energy Dispersive X-Ray (Indirect)

Infrared Spectroscopy (Qual.-Semi-quant./Indirect)
Electron Microprobe Analysis (Qual/Indirect)
Transmission Electron Microscopy (Qual/Indirect)
Ion Microprobe (Qual/Indirect)
Optical Microscopy (Qual-Semi-quant/Direct
Thermometric (DTA/TGA) (Semi-quant/Direct)
Mossbauer Spectroscopy (Semi-quant/Direct)
Others-Raman, EXAFS
Normative Analysis (Quant/Indirect)


CA(OH)2
WHIT
Tooth
HA
Cort. ashed
Cort. ED
Valve



Calcium phosphate inclusions in breast tissue



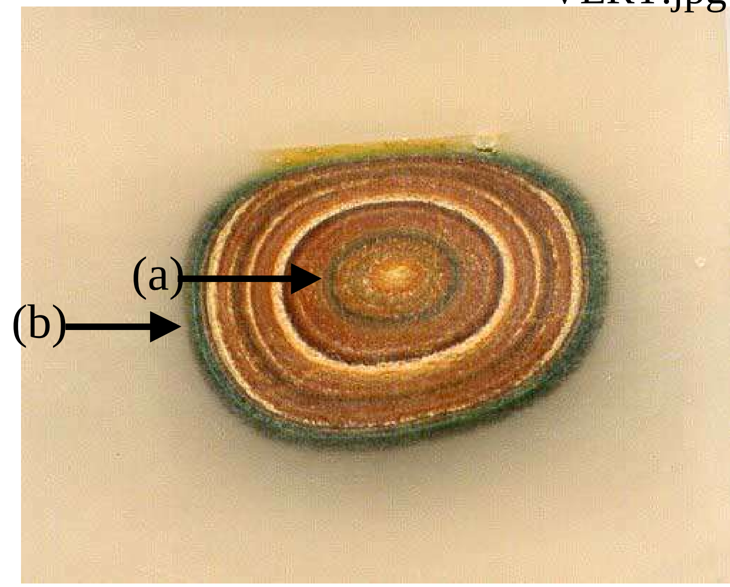
Utilisation d’un marqueur pharmaceutique (MICTASOL BLEU) pour mesurer la vitesse de croissance *in vivo* d’une lithiase vésicale

BLANC.jpg

Oxalates de Ca (whewellite + weddellite) (couches blanches)

Grand diam.=9,5 mm
Lame mince, lumière transmise

VERT.jpg



Acide urique (couches brunes) + phosphate de Ca (couches blanches)

Grand diam.=12 mm
Section polie, lumière réfléchie
1ère prise de MICTASOL BLEU: 23/7/1974 (a)
Dernière prise: JUIN 1984 (b)
Intervention chirurgicale: 24/7/1984
→ Vitesse de croissance radiale=5 mm/10 ans

ULB-Laboratoire de Géochimie-Minéralogie

pilot area

Environmental Risk Assessment Map of the Slovak Republic