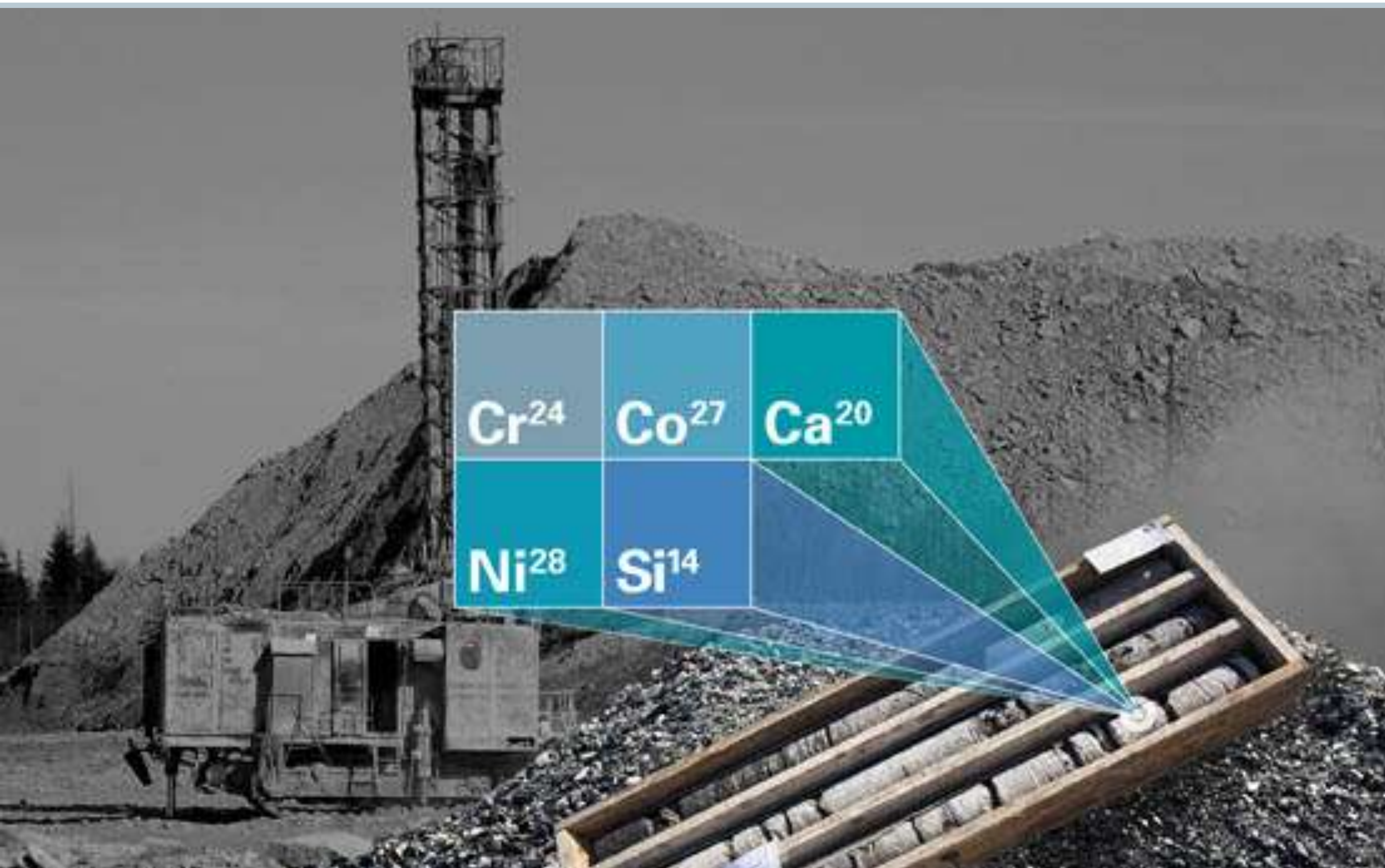
pXRF Solution for Geochemistry, Mining and Exploration

Dipl.Min. Alexander Seyfarth, Dr. Bjorn Klaue

Johannesburg South Africa IMA 2014

Sept 3rd 2014



Analytical Instruments for the Geoscience and Mining Segment....

BRUKER provides a wide range of instruments for the Minerals and Mining Industry

Elemental analysis

- XRF (ED XRF, WD XRF, TXRF, HH XRF, uXRF, EDS)
- Combustion Analysis (C, N, O, H)
- ICP – MS
- OES (Arc & Spark) for solid metal analysis

Compound analysis

- XRD
- GC (and GC-MS) (gas)
- IR (FT-IR and NIR)
- Raman (pRaman, HH Raman)

Other

- Micro CT
- SCD
- AFM
- Tribology


XRD-D2 Phaser


WD-XRF S8 Tiger

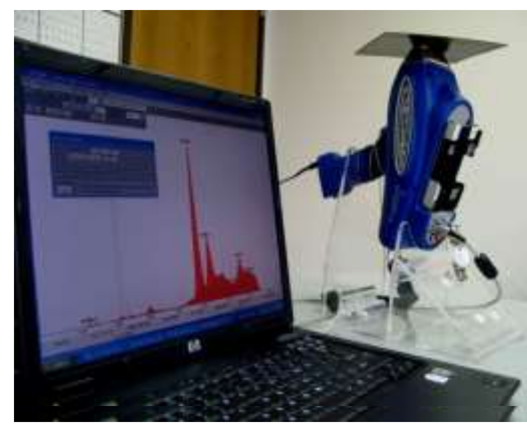

ED-XRF S2 Ranger


HH-XRF

We started with metals as well, only with the hardest one first… 2006…

- Development of HH XRF in conjunction with NASA for PMI on shuttle components and other materials for space exploration and travel (TRACER III V)

Jan 2006: The Space Foundation announced today that KeyMaster X-ray fluorescence (XRF) is officially recognized as a Certified Space Technology (tm). KeyMaster Technologies, Inc., of Kennewick, Wash., developed the XRF analyzer to perform on-the-spot chemical analyses. NASA enhanced and used it on Space Shuttle Discovery to determine the composition of aluminum alloy parts to an accuracy of four decimal places.



From the OEM to a full line of industrial and academic Instruments

INDUSTRIAL

2014

S1 TITAN 600,800 (SDD)
S1 TITAN 200,300 (SiPin)

2012

S1 TITAN LE (SDD)
S1 TITAN SP (SiPin)

2009

S1 SORTER
2 Models

2008

S1 TURBO
3 Models

ACADEMIC – RESEARCH

2014

CORESCANNER + He Mode

2013

TRACER III SD VISON (Camera)

2012

SampleChanger

TRACER III V+

2010

2008

TRACER III SD
TRACER IV SD

2006

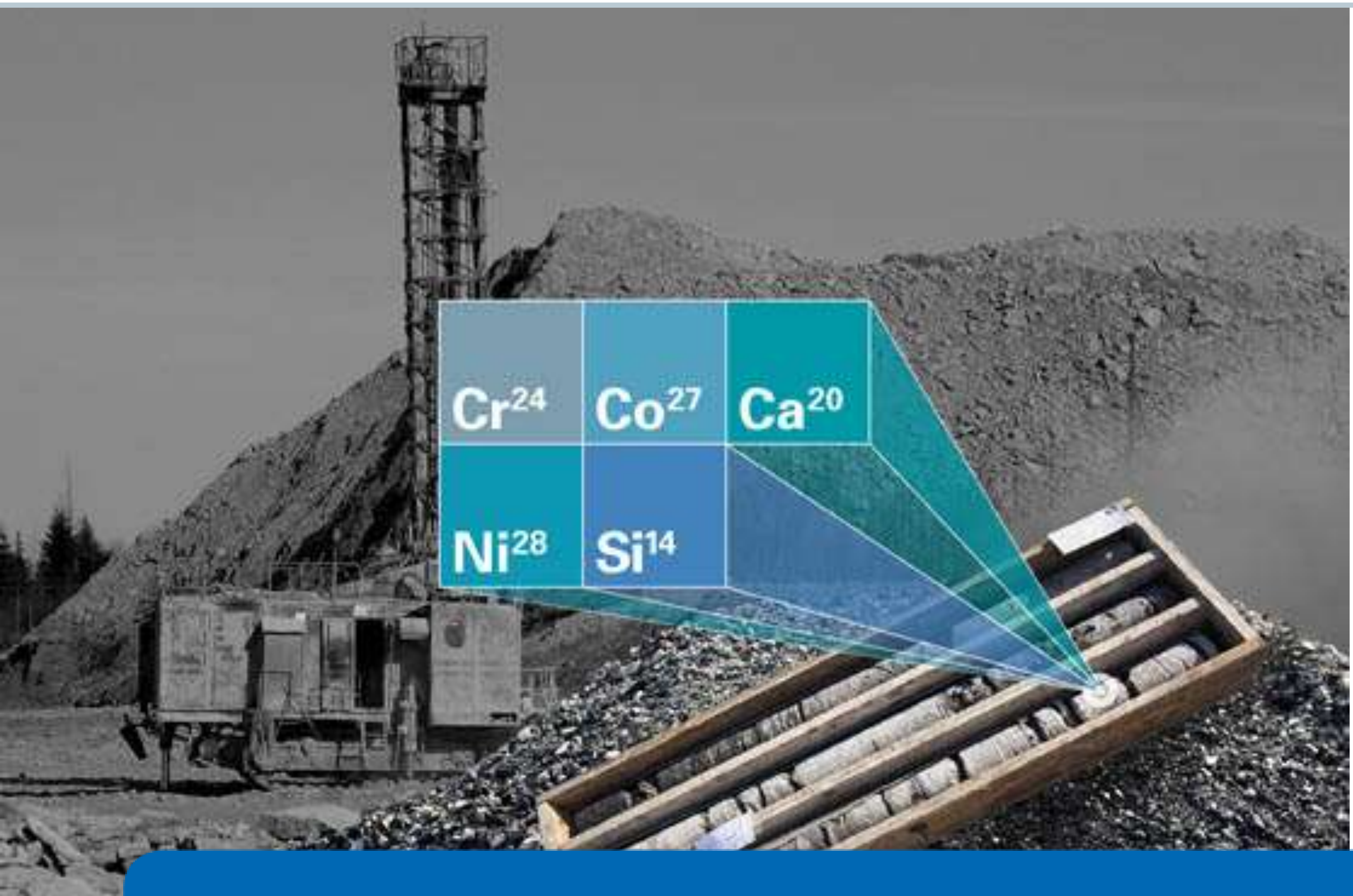
TRACER III V

pXRF Solution for Geochemistry, Mining and Exploration

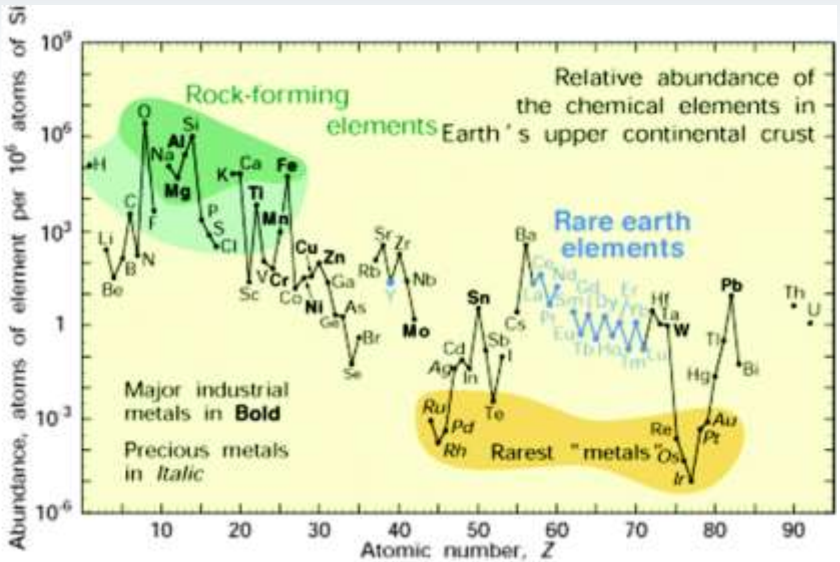
Dipl.Min. Alexander Seyfarth, Dr. Bjorn Klaue

Johannesburg South Africa IMA 2014

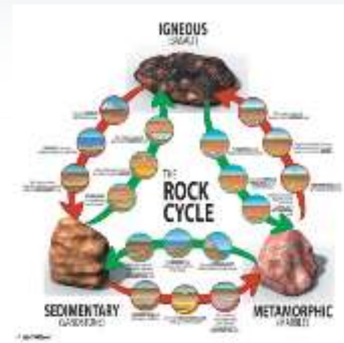
Sept 3rd 2014

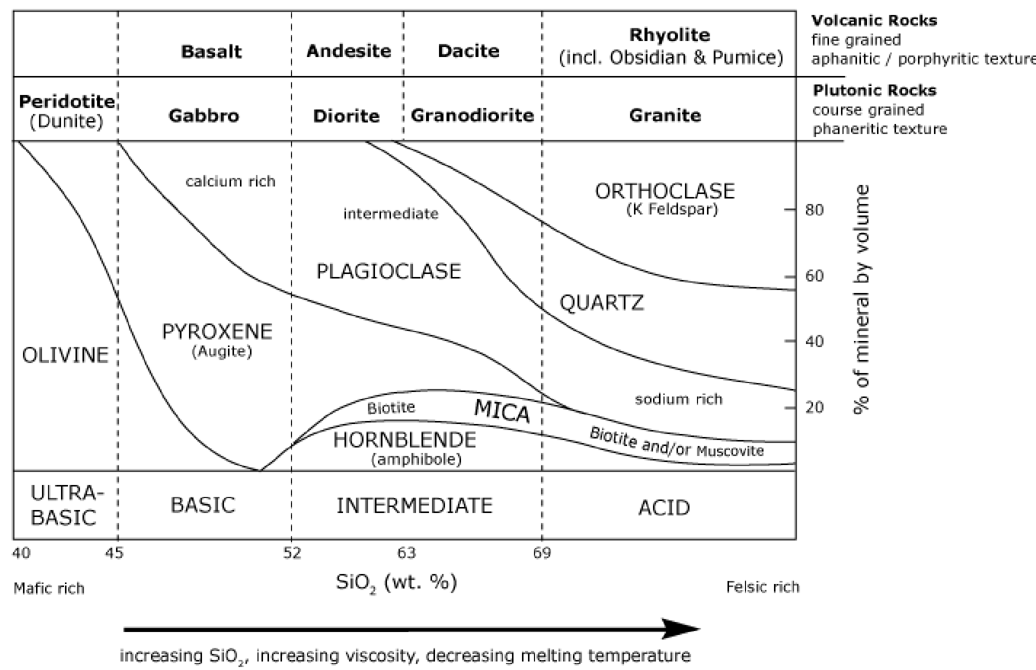


Variability of Geo materials



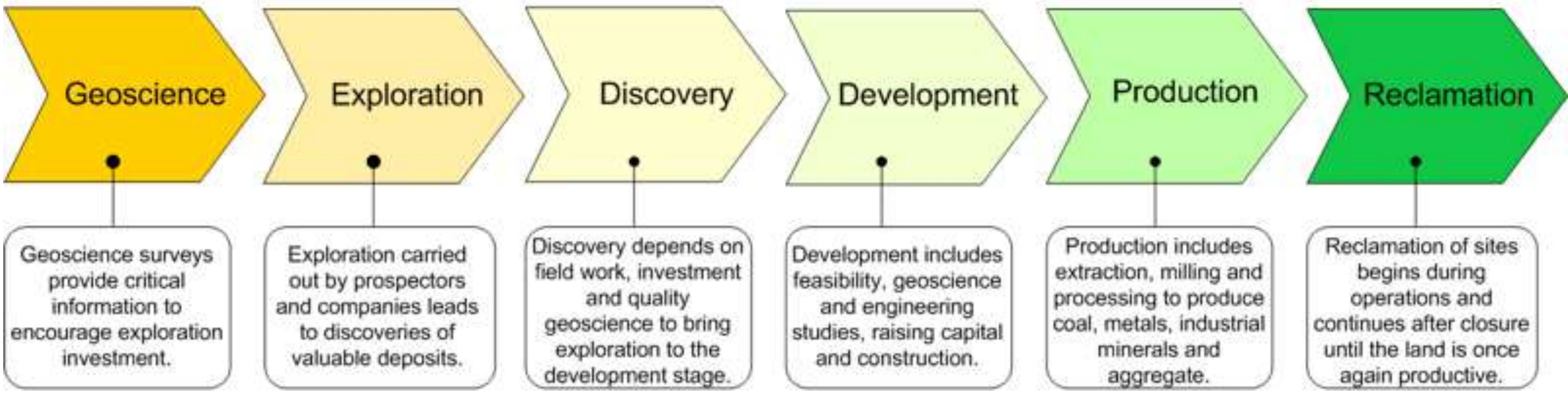
- Highly variable with hundreds of different matrices
- Wide(st) ranging content for many elements





XRF in Mineral Applications
Where?

- Academic / Research segment (Geoscience, some Exploration "mapping")
- Prospection / Reclamation segment
- Development / Production segment



Handheld XRF can be used in all the phases of mining.

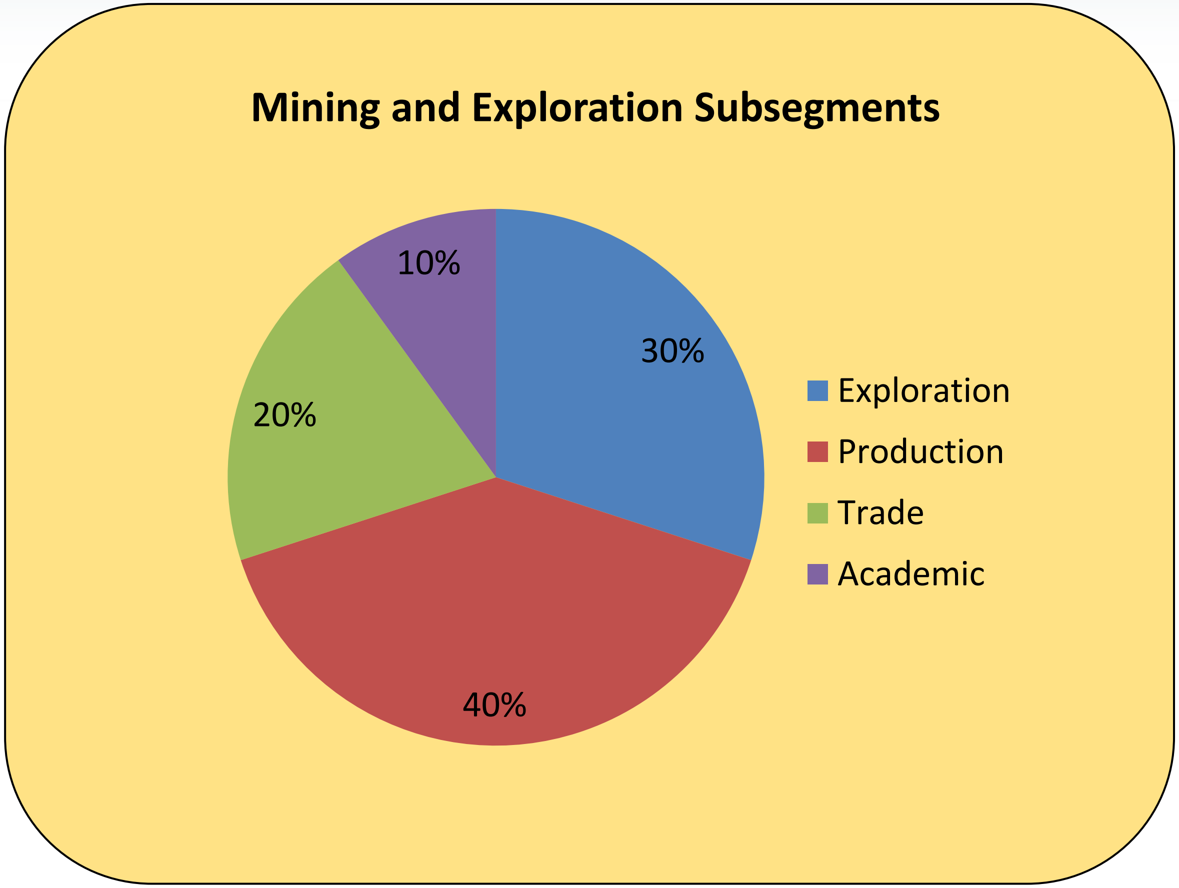
HH XRF in Mining Applications
Why?

- **Key Selling Points/Drivers for HH XRF:**
  - **Logistics, particularly remote locations**
  - **Low cost of analysis & instrumentation**
  - **Low qualification of operators**

Science → Exploration → Production → Trade → Remediation




Overall HH XRF Geo Market Application Distribution



Pay Back of pXRF
What Literature has to say…

- The use of this onsite FPXRF method has been objectively demonstrated to be three times more cost-effective than conventional methods of collecting judgmental samples for subsequent laboratory analysis (Taylor et al., 2004). The real value goes beyond this cost savings. Onsite use of the FPXRF allows an accurate appraisal of a property, ore grade, drill cuttings, cores and concentrates in real time when and where correct decisions are needed.

- Glanzman, Kloos in "Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration" edited by B. Milkereit, 2007, p. 291-301

- Taylor, P.D, Ramsey, M.H. and Potts, P.J., 2004, Balancing Measurement Uncertainty against Financial Benefits: Comparison of In Situ and Ex Situ Analysis of Contaminated Land: Environ. Sci. & Tech., 38, 6824-6831.

Handheld XRF Applications
Academic/Research

- Typical Geochemical field or lab based Analysis for traces or majors (similar to the "big" XRF) using either powders or pellets
- Calibrations can be factory based and can be extended by customer adding own samples or are FULLY customer made using a wide range of preparations or even direct measurements
  - Generic (Powder/Pellet) Applications: Canada Geo Survey (general mapping), University of Western Ontario (search of impact structures)
  - Direct Measurements: Basalt direct rockface/outcrop measurement of s for mapping different eruptions (WSU) Obsidian, Chert et al for sourcing not via Fingerprinting but traceable to international samples (E.g. MURR)
  - Liquid Measurements: Analysis of brines and Mine discharges
  - Filter Measurements: Airquality Filter , Ion Exchanger Filters

Having made your own Calibration and showing all details on it Allow ORIGINAL PUBLICATIONS in peer reviewed Journals

Handheld XRF Applications
Exploration

The pXRF analyzes the **geochemistry** of soil, sediment, and drill core samples in the field.

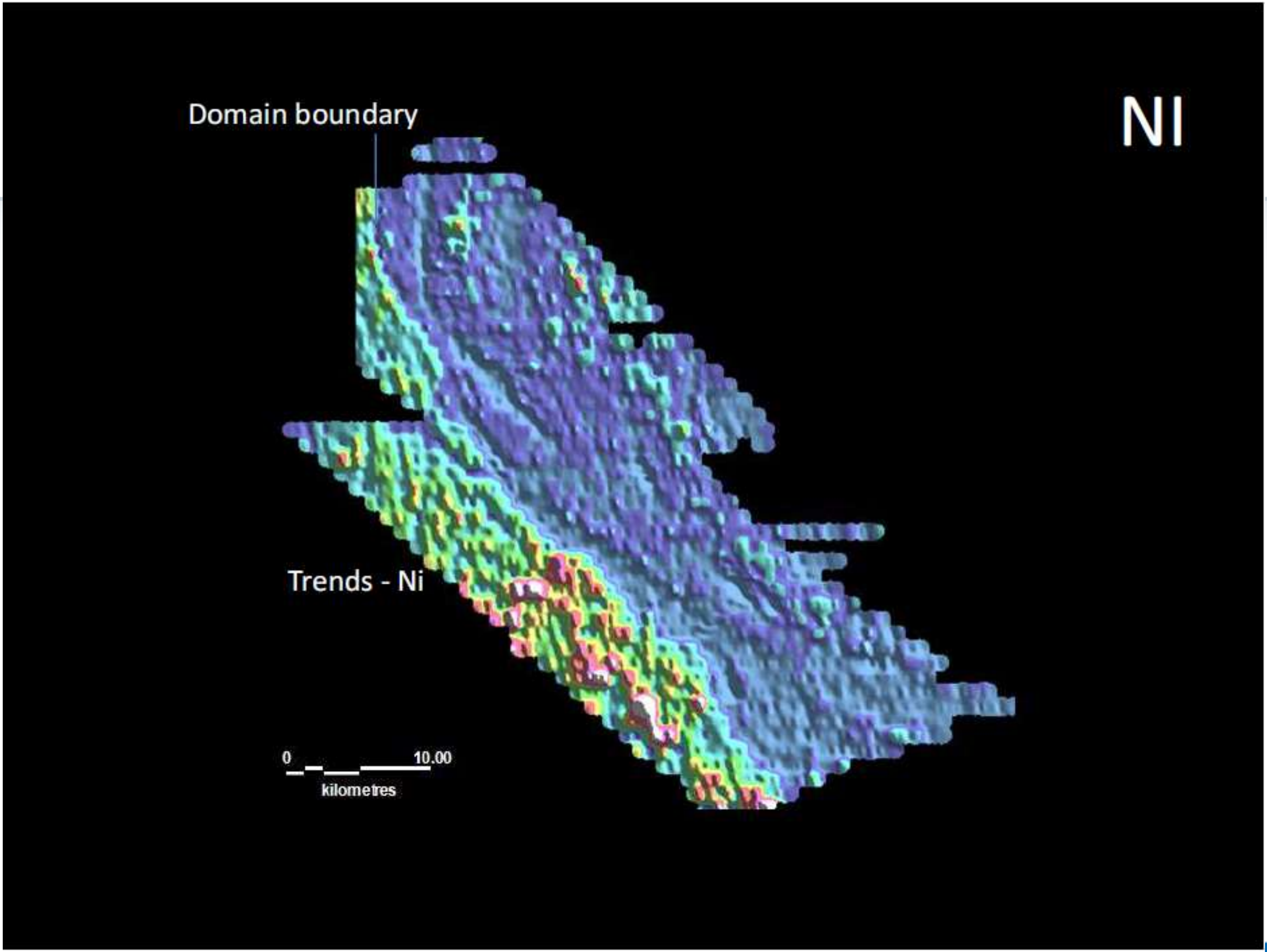
- Object is to capture spatially resolved data and look for concentration “differences” or trends
- This helps to guide and expedite ore exploration and research projects
- Mostly non direct on pulp or powdered samples

Geochemical Mapping

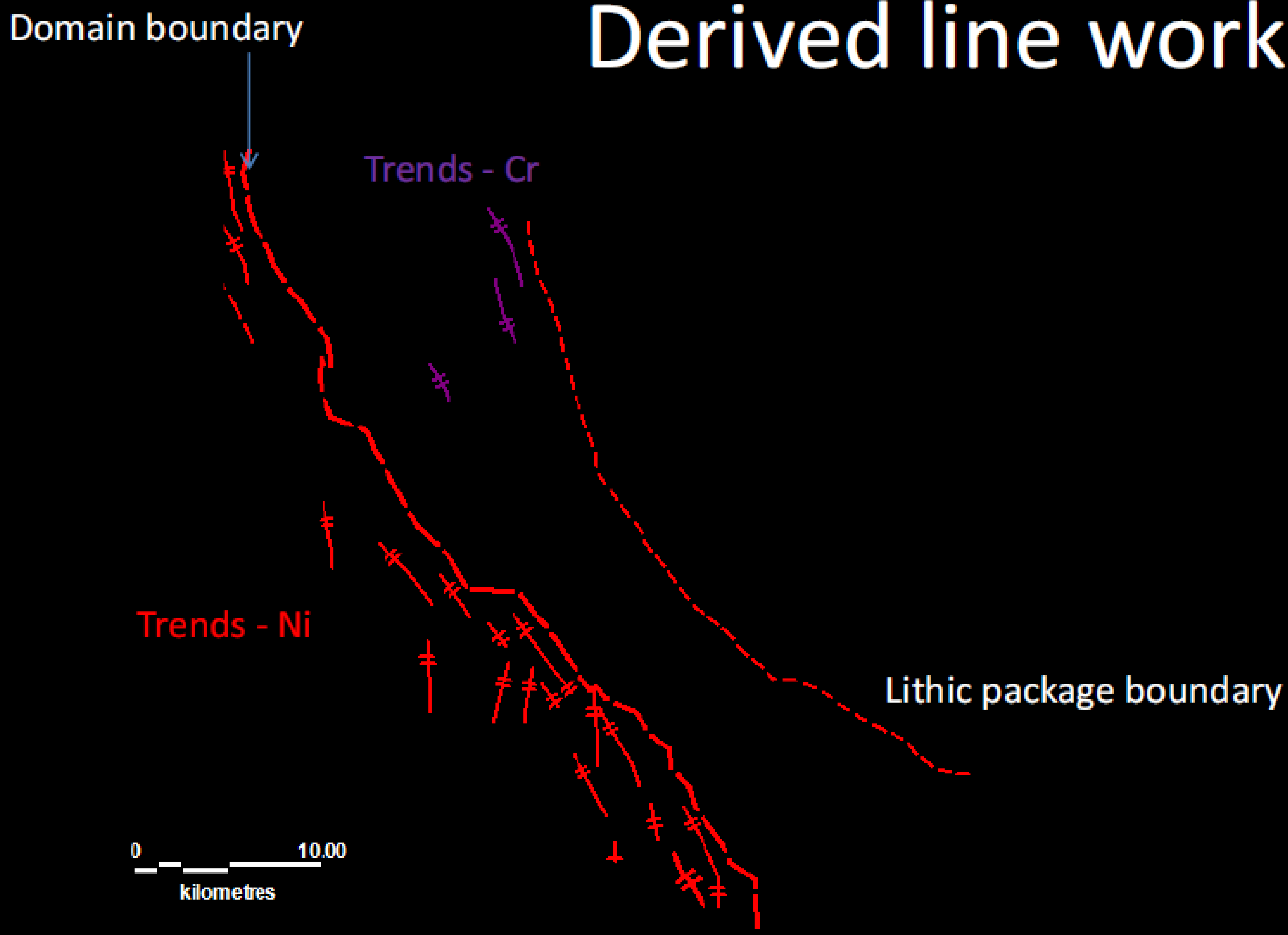
There is a LOT of detail and information in each element

Dr Nigel W Brand

26th IAGS: Rotorua, NZ
Portable XRF (*pXRF*) in mineral exploration: state of the art in 2013: Workshop
17th November 2013


Domain boundary
NI
Trends - Ni
0
10.00
kilometres

Derived line work



Handheld XRF Applications Operations/Process (1)

- Floatation/processing trouble shooting
  - New or "repaired" circuits can be brought online faster with onsite pXRF analysis
  - Chemicals dosage checks
- Grinding control / Grinding tests
- Tailings check
- Predictive Maintenance
- Positive Material Identification
  - E.g. is the wear resistant material ordered really "wear" resistant or a knock off

Handheld XRF Applications
Operations/Process (2)

- Grade delineation for production area optimization
- Blast Hole analysis: Quality data from drill powder
  - Faster data with ability to “map”
  - pXRF link to laboratory data with data reprocessing
- Lab on a Rig




Handheld XRF Applications
Industrial Minerals/Cement/Gypsum

- Limestone, Calcium carbonate (**$CaCO_3$**) is one of the most versatile minerals found in the earth's crust. Physical properties and low processing cost makes it the most widely used filler material.

- Handheld XRF can be used to measure Calcium carbonate composition directly from rock or from quarry. This information can be used to effectively control mining and excavation process.

- Sand and Feldspar grade and Fe control

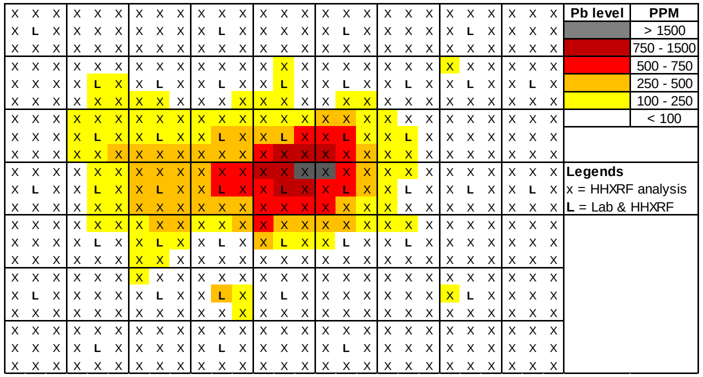
- Gypsum and Cement

Handheld XRF Applications
Traders, Inspection

- Getting “reliable” data for purchase from “artisanal” mining
- Variable Sample presentation and ranges from concentrate to industrial mineral
- “tuned” to the commercial lab data
- “conflict” source identification (or obfuscation)

Handheld XRF Applications
Mine Site Reclamation

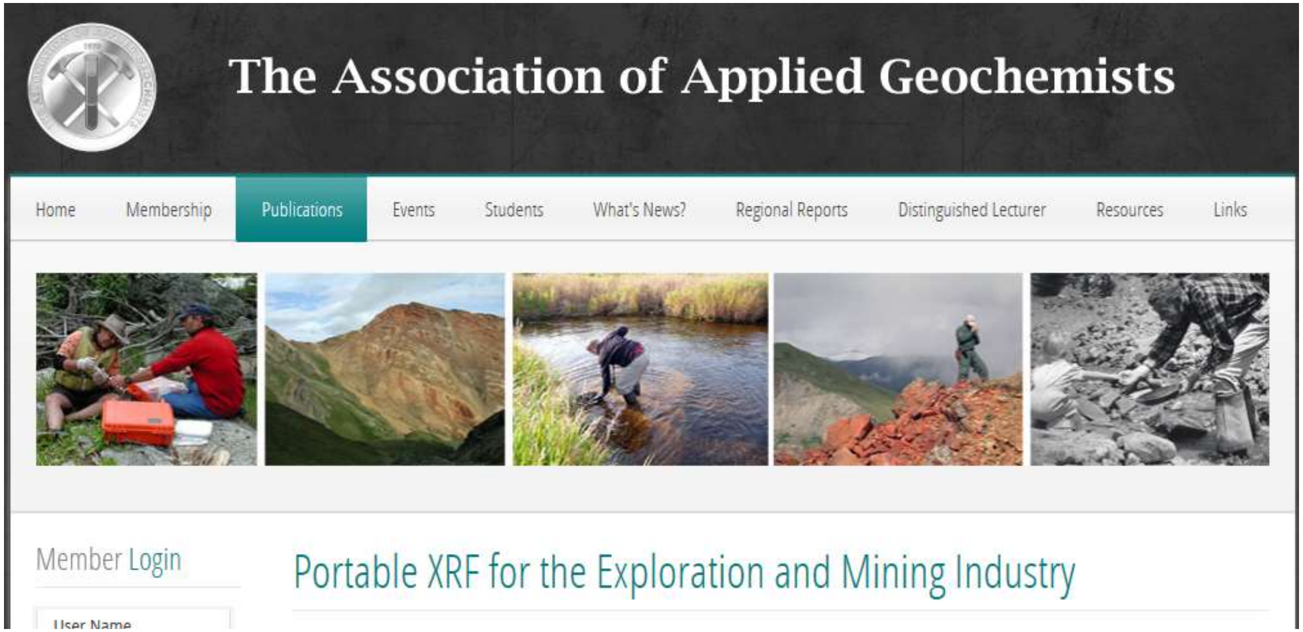
- Reclamation and clean-up of abandoned mining sites requires rapid field decisions to be able to coordinate the process effectively.
- pXRF provides a fast and inexpensive approach to site characterization for identifying heavy element pollutants in soil.
- By storing GPS coordinates with the data acquired ON the unit it is possible to quickly map the contaminated area (e.g. Google maps) or import it in any GIS



CAMIRO Project
Demystifying pXRF
Procedures and Capabilities

BRUKER

CAMIRO
Canadian Mining Industry Research Organization



CAMIRO I and II 2010/2011

- **10E01/ 11 E01 Quality Control Assessment of Portable XRF Analysers: Development of Standard Operating Procedures, Performance on Variable Media and Recommended Uses**
- Investigators: Gwendy Hall (Consultant), technical assistant, commercial laboratories (including ALS, SGS),
- Participation of PXRF manufacturers: **Bruker. Olympus InnovX, Thermo Fisher Scientific**
- Need for set of rock standards and procedures to evaluate and test variability of data from hand-held instruments.
- Phase 1: variations in element data from certified reference material powders (Startup October 2010; Completed June 2011)
- Phase 2: variations in element data in rocks, core, soils, tills and water saturated soils vs. powders. (Startup January 2012; Completed August 2012)

Performance Comparison of Portable XRF Instruments:

A Mineral Exploration Prospective

Presented by

Dr Nigel Brand

26th IAGS: Rotorua, NZ

Session 8A: Sampling &Real Time Analysis

19th November 2013

Some Lessons Learned from CAMIRO and pXRFS Benchmark

- All pXRF follow the laws of physics with respect to sample homogeneity: The analyzed layer and grain size is affected by the mineralogy and chemistry. With decent samples you CAN get decent results
    - Samples should to be prepared as FINE powder and PE (e.g. PROLEN™) foil should be used to enable light element analysis
- High Variability between the vendors installed "black box" application due to different "design" approaches
- "PRECISE YET INACCURATE"
- High Variability between Instruments: "INDIVIDUAL & UNIQUE"
- Vendor Difference in sensitivity (due to design approach) and selectivity

GEO Instrument Capabilities Hardware:

- All major vendors use high end Silicon Drift Detectors of varying sizes (size does ONLY matter for the sensitivity for light elements)
- Geo application require a higher resolution than alloy applications (the lower the eV number the better) BUT it is a function of count rate and therefore needs to be seen in context
- Optical Coupling e.g. distance from sample to detector determines sensitivity especially for light elements: It also affects power settings and “emissions”.
- Most units run now on 50 kV: Which targets are used and which applications are available on the target
- Check for moving components which can get exposed to “sample” can cause breakdowns and require maintenance
- Protection against sample ingress, which can cause detector breakages needs to seen in context with analytical requirement

GEO Instrument Capabilities Software

- How is unit standardized (Gain control) ?
- GUI suitable for designated user group/ language?
- Different Levels of access: Who can do what?
- Data integrity: How is data stored and what is stored with the data?
- Reporting and data transfer options
- Can data be recalculated?
- Results display with Analytical Error , Spectrum access
- Connectivity (BT,WIFI,USB)
- Customization: How can a method be customized?
- Calibration: Can a user calibrate and if so how and with what options….

GEO Instrument Capabilities
Calibrations / Applications

- What Calibrations/Apps are available?
- How many different beams / phases are being used?
- What is the recommended timing to asses throughput?
- Which elements and ranges are covered?
- LOD information based on which matrix ….
- What is the App designed for (exploration, grade control)?
- What is the default preparation?
- How can the Application be modified ?
- Ability to making your "own" ?
- Ability to get custom applications on in type materials?

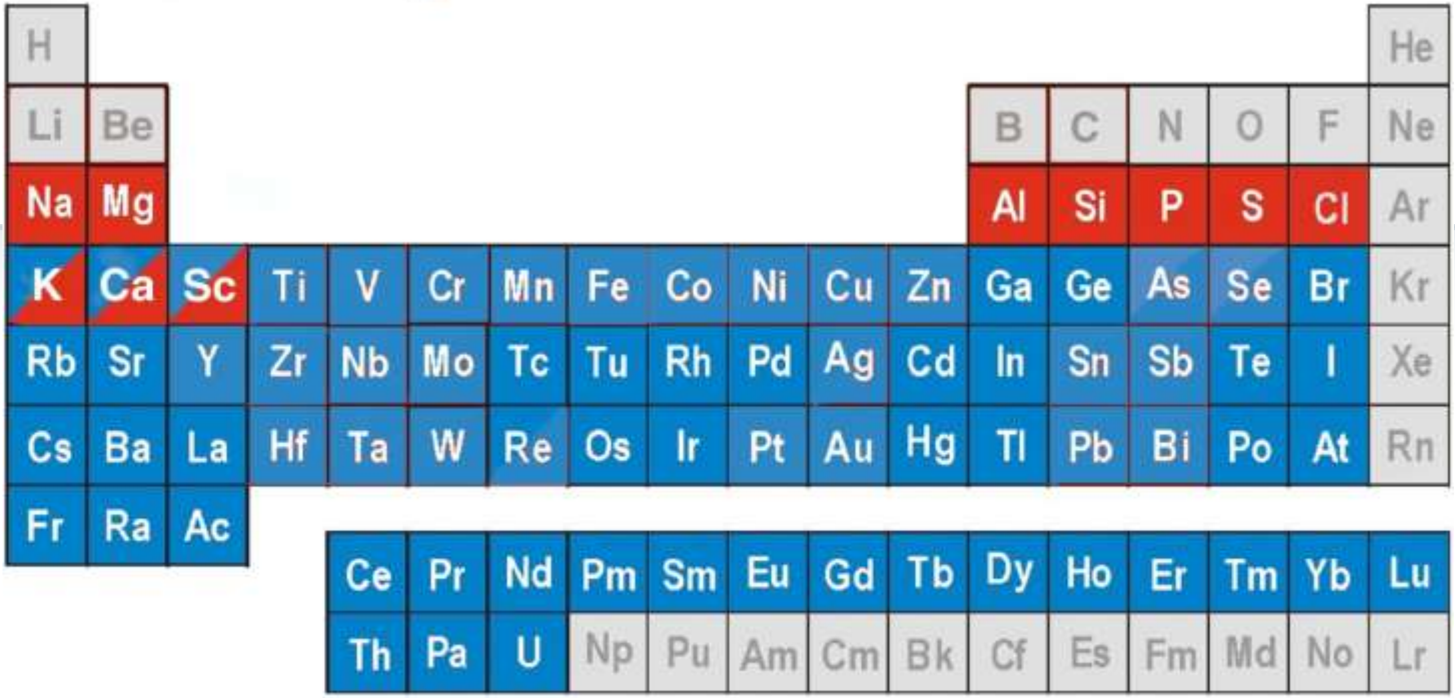
What is the biggest problem for pXRF?

SAMPLING and SAMPLE

Sampling and Sample Preparation … 90% of YOUR success

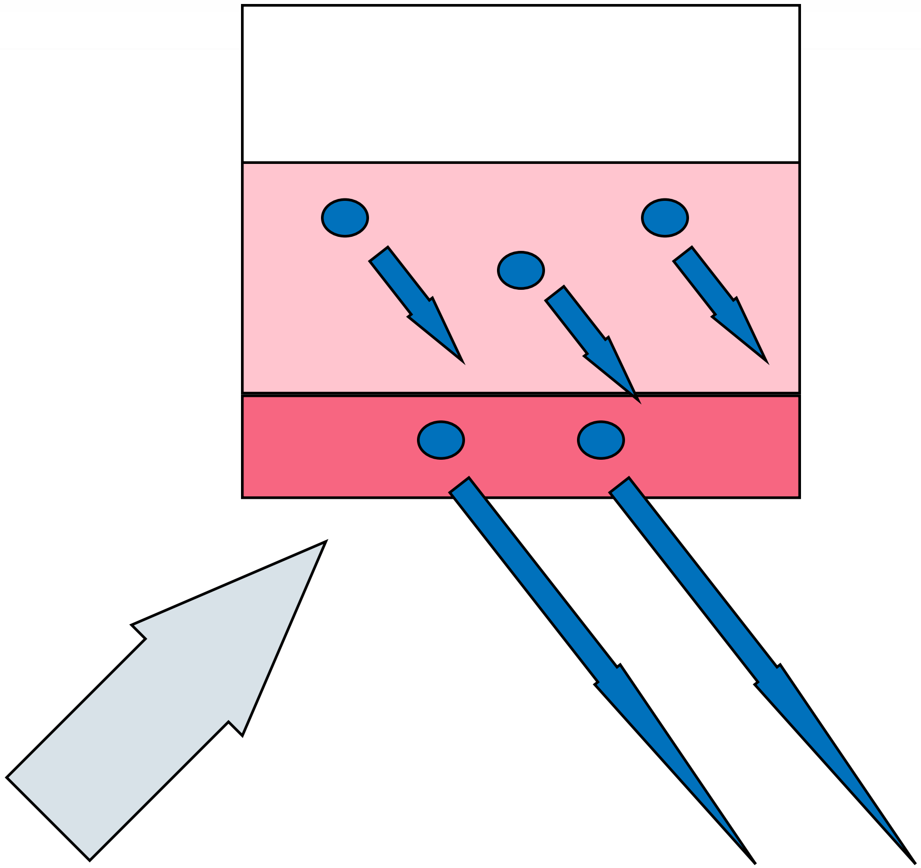
Sampling Considerations

- Heterogeneity
- Grain size
- Moisture content
- Measurement depth
- Sample bag and film material
- Sample Presentation



Transmitted	Air ~10%	Air > 50%		Air > 90%			Kapton >90%		
Line	1 kV	2 kV	3 kV	4 kV	5 kV	6 kV	7-10 kV	10-20 kV	20-30 kV
Ka	Mg, Al, Si	P, S, Cl		Ca, Ti	V, Cr	Mn	Fe, Co, Ni, Cu, Zn	Sr, Y, Zr, Nb, Mo	Ag, Cd, Sn, Sb
La		Zr, Nb, Mo	Ag, Cd, Sn, Sb				Hf, Ta, W, Au, Hg	Pb, Bi,	

Analyzed Layer of a Sample



- No excitation within the inner (upper) part of the sample
- The lower parts (layers) of the sample can be excited by short wavelengths, but emitted radiation will be absorbed within the sample
- Fluorescence radiation to be measured comes from a layer near the sample surface

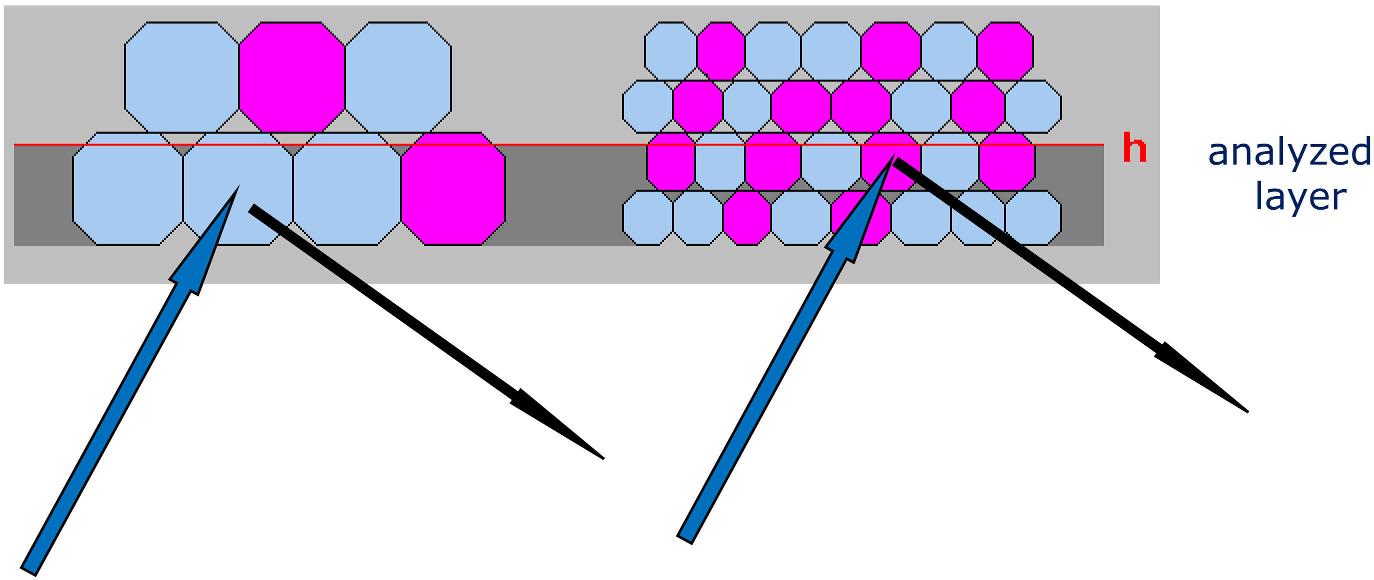
Saturation Depths in Different Matrices

Line	Energy	Graphite	Glass	Iron	Lead
Cd KA1	23.17 keV	14.46 cm	8.20 mm	0.70 mm	77.30 µm
Mo KA1	17.48	6.06	3.60	0.31	36.70
Cu KA1	8.05	5.51 mm	0.38	36.40 µm	20.00
Ni KA1	7.48	4.39	0.31	29.80	16.60
Fe KA1	6.40	2.72	0.20	* 164.00	11.10
Cr KA1	5.41	1.62	0.12	104.00	7.23
S KA1	2.31	116..0 µm	14.80 µm	10.10	4.83
Mg KA1	1.25	20.00	7.08	1.92	1.13
F KA1	0.68	3.70	1.71	0.36	0.26
N KA1	0.39	0.83	1.11	0.08	0.07
C KA1	0.28	* 13.60	0.42	0.03	0.03
B KA1	0.18	4.19	0.13	0.01	0.01

0.01 µm = 10 nm = 100 Å

atom radius: 0.5 - 3 Å

Particle Size Effects of Heterogeneous Powder Samples



Particle Size Effects of Heterogeneous Powder Samples

Compound	Line	Concentration [%]	Energy [keV]	Layer Thickness [µm]
Fe_2O_3	Fe KA1	0.722	6.40	**174**
MnO	Mn KA1	0.016	5.89	**139**
TiO_2	Ti KA1	0.016	4.51	**66**
CaO	Ca KA1	30.12	3.69	**104**
K_2O	K KA1	0.103	3.31	**77**
SO_3	S KA1	0.000	2.31	**27**
P_2O_5	P KA1	0.004	2.01	**19**
SiO_2	Si KA1	1.130	1.74	**13**
Al_2O_3	Al KA1	0.277	1.49	**8**
MgO	Mg KA1	21.03	1.25	**7**
Na_2O	Na KA1	0.029	1.04	**4**
CO_2		46.37		

Thickness of the sample from which 90% of the measured intensity is derived

NBS 88b Dolomite

Pressed pellet without binder

Especially for the lines of light elements,

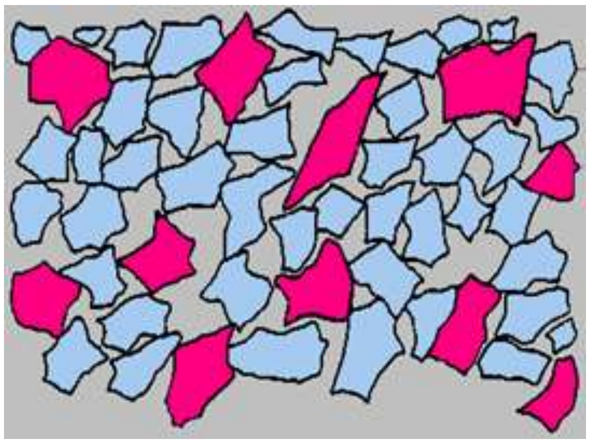
average grain size ≈ layer thickness

(typically grain sizes vary between : 20 - 200 µm)

Grinding accessories…
Field

Angle Grinder for direct rock face sampling

Preparation as Loose Powder



- Powder sample is placed into a liquid sample cell with a suitable window and measured
- Particles have air gaps between them
- Arrangement of particles and air gaps is not reproducible
- Suitable when analyzed layer depth is very large (energy of line is high)
  - Example: Fe KA1

Analysis of Prepared Samples

- Most accurate results are always achieved by uniformly homogenizing the samples and preparing them for sample cup analysis.
- Particle size, sample homogeneity, sample moisture and sample thickness are factors which may affect instrument accuracy.
- Grind to less than 75 um or < 200 mesh
- 4µm Prolene film should be used

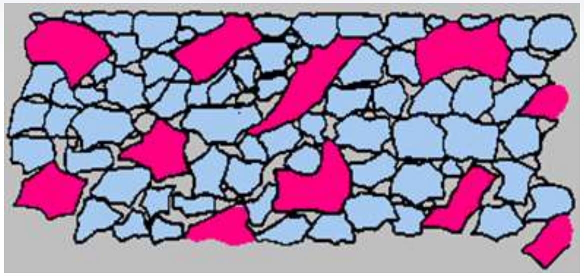
Different sample cups

1530 cup with 1630 lid
31mm/23mm/24mm

Exploration
When screening and speed is key…

- Simple plastic bags (checked for contamination) are also good sample containers. Recommended sample bag is thin freezer bag – type LD-PE plastic bag. Paper bags are also possible
- Samples can be measured directly through the bag. Notice, that measurement through the sample bag may effect on results depending on measured elements and thickness and material of the bag.
- Light element analysis is not possible through the sample bag – sample bag material will absorb the signal of light elements (Mg, Al, Si, P, S, Ca, K, Ti, V).
- Depending on the material and thickness of the sample bag, Cr is generally the lightest element that can be measured through a sample bag.
- Sample thickness should be min. 1cm (1/2”).
- If sample is non-homogeneous, several measurements should be made for averaging.

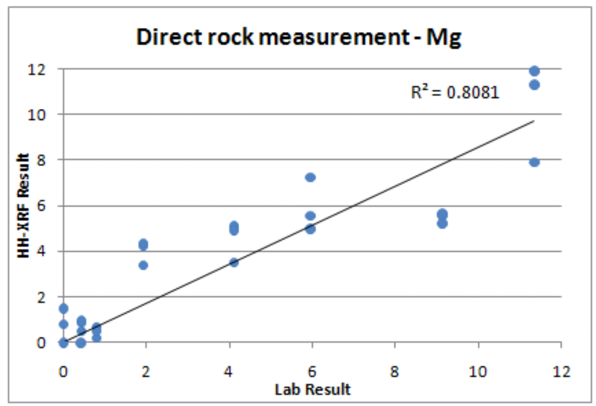
Preparation as Pressed Pellet

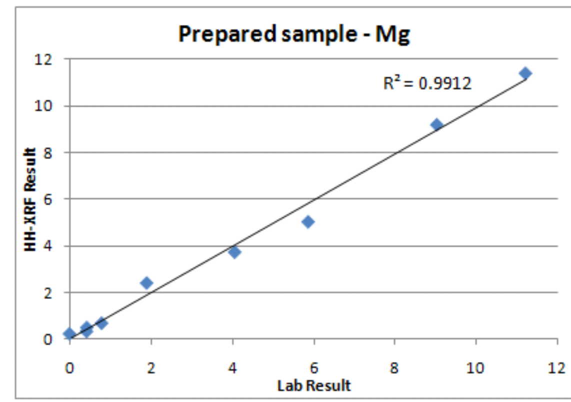


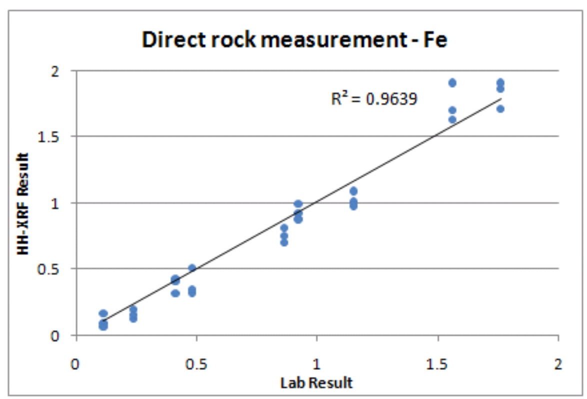
- Powder is compacted under high pressure
  - Typical pressure is 5 to 30 tons
  - Typical holding time is 10 to 30 seconds
- Makes arrangement of particles and air gaps very reproducible
- Samples are typically pressed into aluminum cups
  - Provide support for samples
- Alternatively samples can be pressed onto a support material
  - Like Cellulose or Boric Acid
- Samples may need the addition of binder to aid in forming a strong finished pellet

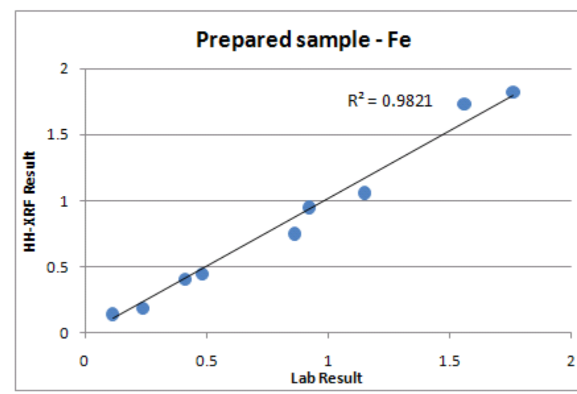
Direct rock measurement vs measurement of prepared sample

- Limestone rock samples were first measured directly with HHXRF.
- Samples were prepared and analyzed with laboratory WDXRF and with handheld XRF
- Results demonstrate challenge of the direct rock measurement.





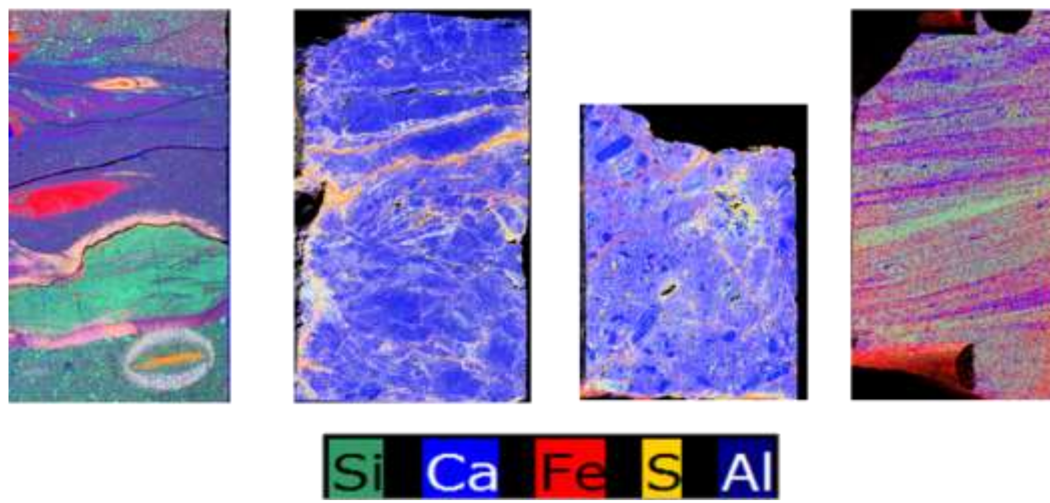




Example: Elemental distribution of drill cores

- Handheld XRF can be effectively used for drill core analysis.
- Quantitative measurement directly from the drill core surface is possible but averaging of multiple measurements is typically required.

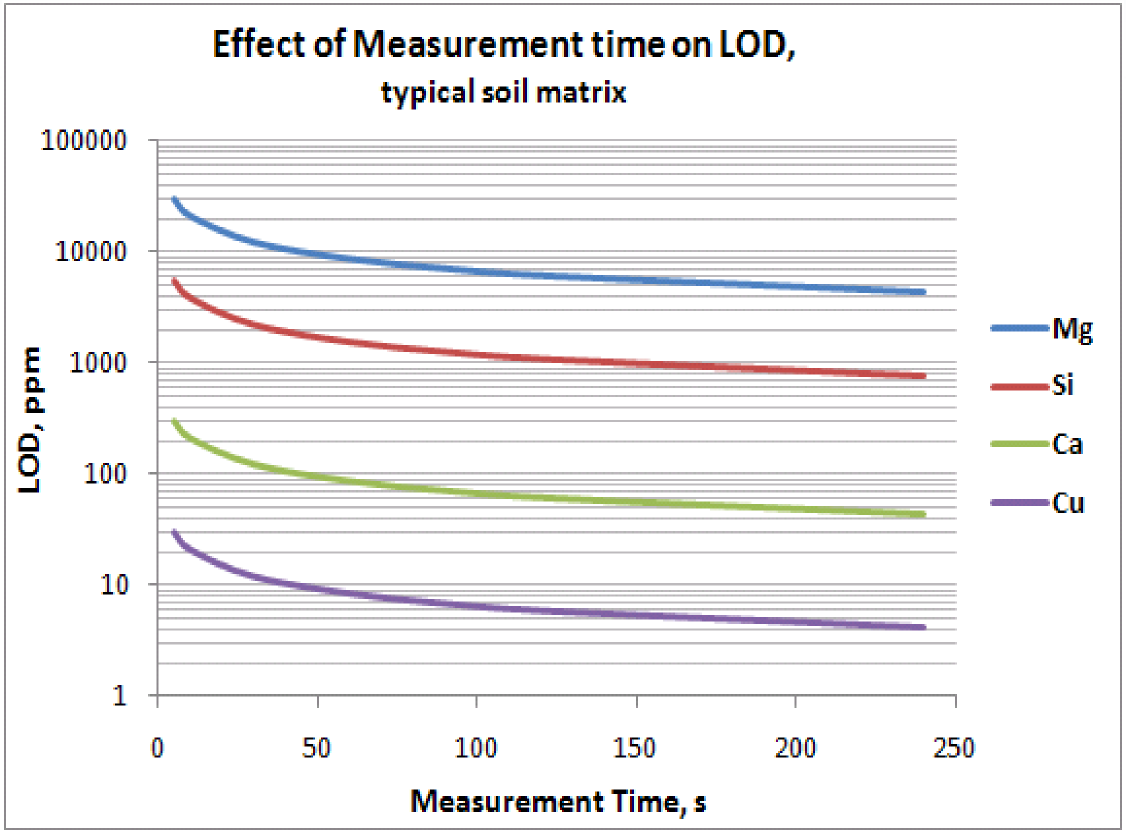
TRACER series



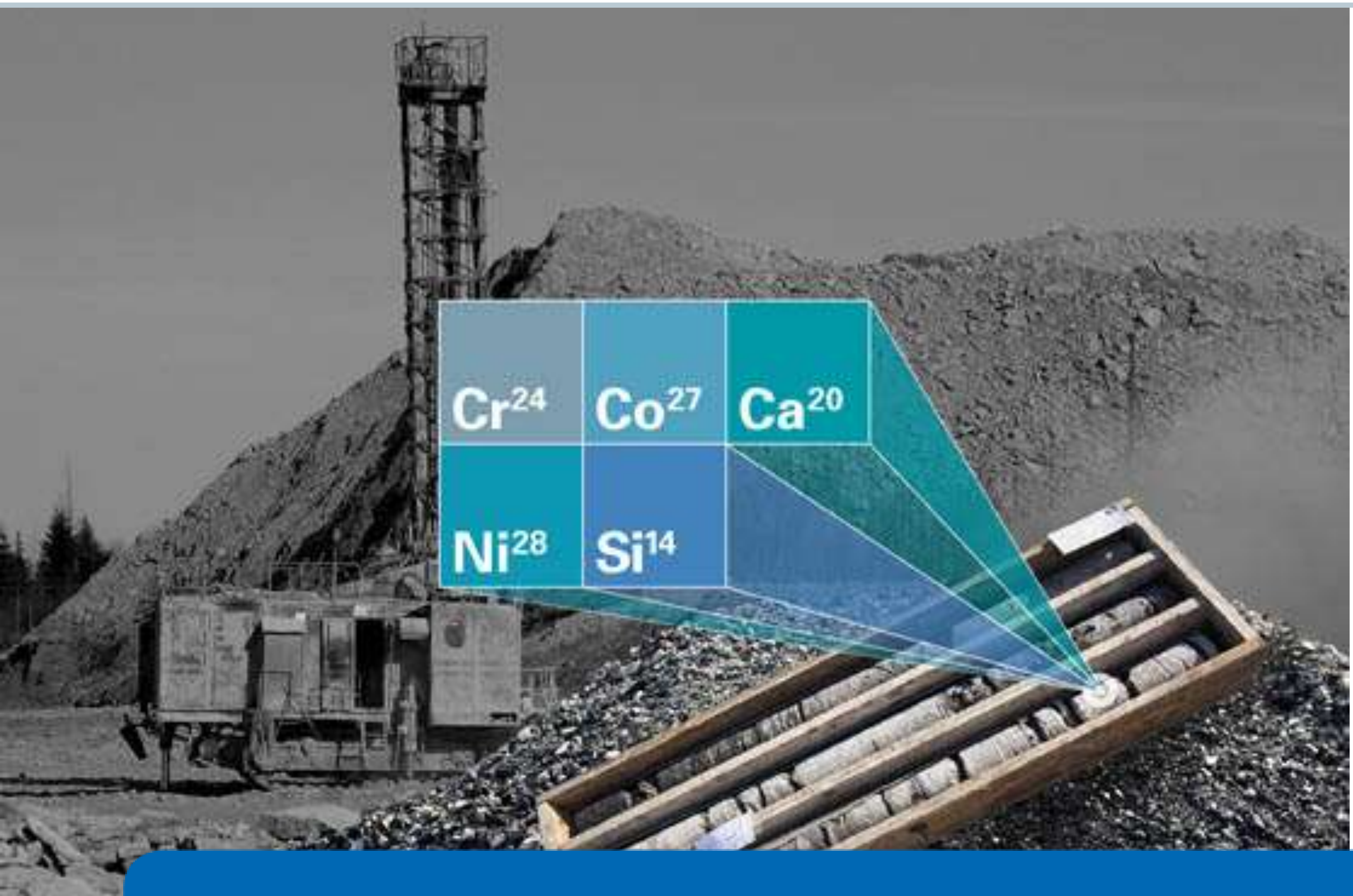
M4 TORNADO

Light element Lower limit of Detection (LOD)

- LOD is the estimate of the smallest concentration which can be detected
- LOD depends on measurement time (sqrt(T)), matrix (including moisture), grain size.
- Generally light elements have significantly higher LOD's than heavy elements, such as Cu.
- Precise measurement of light elements with HHXRF requires relatively long measurement time



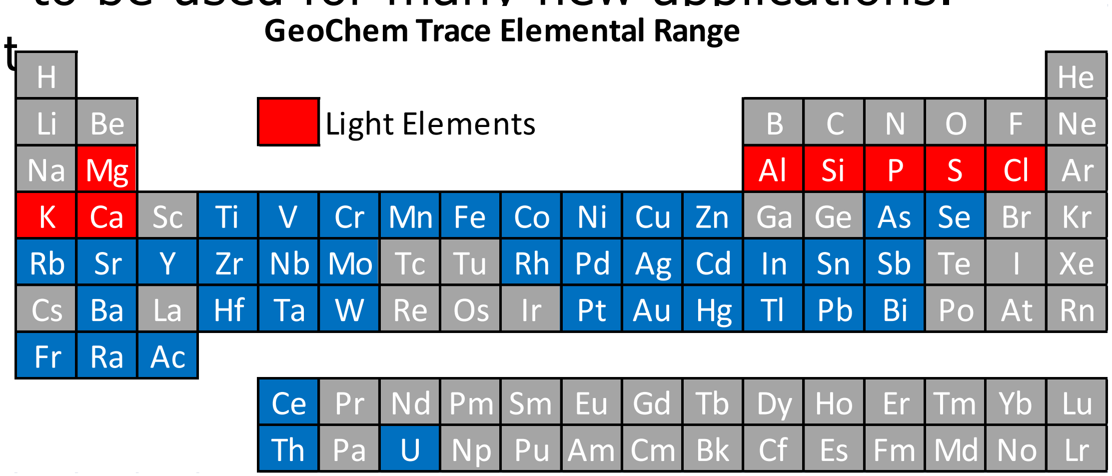
Calibration tuning



S1 TITAN 600,800
Geochem Application

Light Element Analysis

- S1 TITAN 600 analysis range is Mg-U
- For HH-XRF, Mg, Al, Si, P, S, Cl, K, Ca are considered as light elements
- Light element analysis provides important information on sample matrix and enables HHXRF to be used for many new applications.
- Light element also makes t
  more accurate

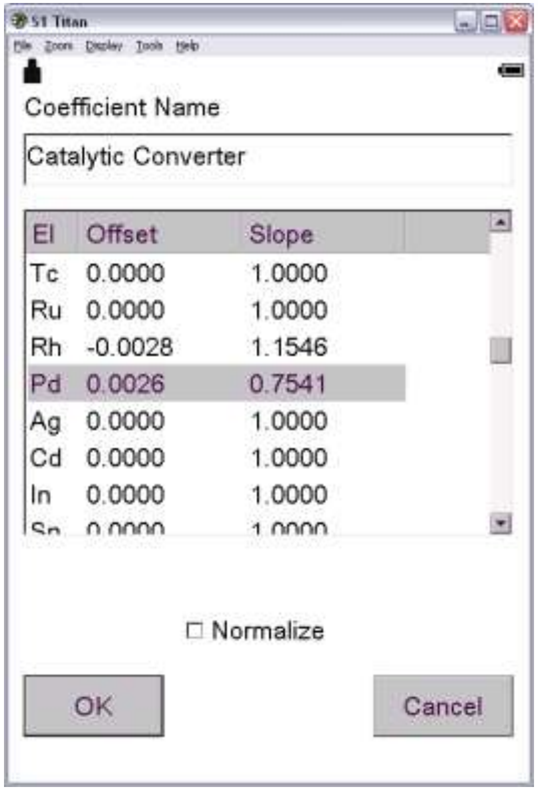


Challenges

- Grain size
- Heterogeneity
- Moisture content
- Measurement depth

Type Standardization Example for S1 TITAN

- Type standardization feature enables user to adjust factory calibrations by setting element-specific slope and offset coefficients with the S1 software.
- This feature is specifically designed for mining applications to enable easy on-site calibration optimization based on known standards.
- In some cases, type standardization can replace customer-specific calibration.
- Multiple coefficient sets can be saved for each calibration, which in practice makes it possible to create “sub-calibrations” for different sample types.



(1) Find a Sample set with reference concentrations….

Reference Sample	Si	Ca	Fe	SiO2	CaO	Fe2O3
FO15-NBS690-powder	1.73	0.14	66.85	3.70	0.20	95.60
FO15-Fe2O3-powder	0.00	0.00	69.93	0.00	0.00	100.00
FO15-MW-1-powder	2.15	0.04	66.08	4.60	0.05	94.49
FO15-606-1-powder	1.04	1.04	59.66	2.23	1.46	85.31
FO15-ICRMP3-powder	1.75	3.19	58.60	3.75	4.47	83.80
FO15-ICRMP4-powder	2.94	2.15	60.20	6.29	3.01	86.09
FO15-SiO2-powder	46.72	0.00	0.00	99.99	0.00	0.00
FO15-681-powder	8.32	2.00	33.21	17.80	2.80	47.49
FO15-680-powder	4.20	0.45	59.98	8.99	0.63	85.77
				* 2.14	*1.4	*1.43

(2) calculate type standardization

S1 Coefficient Calculation 1-3 workshop.xls [Compatibility Mode] - Mi...

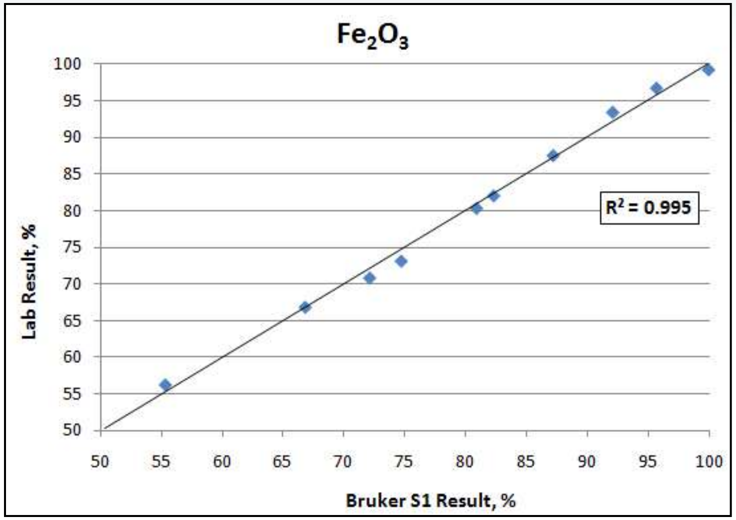
-Correlation indicates agreement between Reference values and S1 Measurement results . Correlat

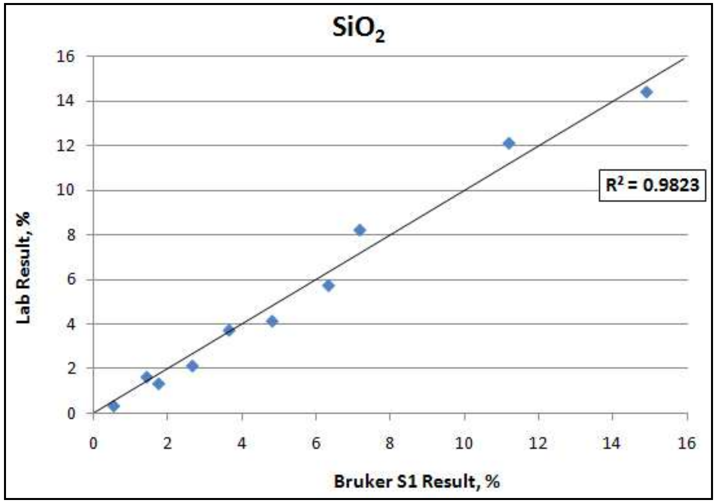
Element 1	Fe2O3		Element 2	SiO2
SLOPE	**1.0253**		SLOPE	**1.0744**
OFFSET	**0.0000**		OFFSET	**-0.7306**
CORRELATION	**99.9%**		CORRELATION	**100.0%**

Reference values	S1 Meas. Results	Adjusted S1 Result		Reference values	S1 Meas. Results	Adjusted S1 Result
95.6	94.04	96.42	nbs690	3.7	5.6	5.29
85.8	85.7	87.87	680	8.99	7.7	7.54
100	97.1	99.56	fe2o3	0	0	-0.73
0	0.08	0.08	SiO2	100	93.65	99.89
47.5	49.15	50.39	681	17.8	17.9	18.50
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73
		0.00				-0.73

Coefficient Calculation | Element-Oxide conversion

(3) get improved results





	Fe_2O_3	Al_2O_3	SiO_2	S	CaO	MnO
Meas 1	87.9	4.31	5.54	0.022	0.093	0.529
Meas 2	87.8	4.54	5.95	0.028	0.093	0.498
Meas 3	86.5	4.69	6.04	0.020	0.083	0.503
Meas 4	88	4.98	6.02	0.025	0.086	0.494
Meas 5	87.3	4.84	6.07	0.019	0.085	0.496
Meas 6	88	4.58	5.47	0.031	0.084	0.495
Meas 7	88.4	4.61	5.91	0.028	0.086	0.497
Meas 8	88.2	4.21	5.81	0.021	0.094	0.503
Meas 9	87.3	4.89	6.02	0.026	0.079	0.502
Meas 10	86.4	4.49	5.9	0.020	0.080	0.502
STD DEV	0.689	0.246	0.209	0.004	0.005	0.010
Average	87.58	4.61	5.87	0.024	0.086	0.502
Lab Results	87.15	4.47	6.35	0.029	0.098	0.439

Calibration
Using your OWN calibrations…

Strategy for Developing and Calibrating Shale and Mudstone Chemostratigraphies using Handheld X-ray Fluorescence Units

Harry Rowe
University of Texas at Arlington

2011 Paper at GSA

Denver X-Ray Conference August 2014

Handheld XRF Applications to Mudrock Chemostratigraphy: Perspective, Methods, Pitfalls, and Examples

Harry Rowe

Bureau of Economic Geology

University of Texas at Austin

Acknowledgements: Henry Francis, Barry Maynard, Sue Rimmer; Bruce Kaiser, Alexander Seyfarth; Steve Ruppel, Bob Loucks, and the Mudrock Systems Research Laboratory, the BEG Administration, Dean Sharon Mosher of the UT Jackson School,; Nestor D Phillips II, all of my students who have helped me look better than I really am…☺

Initial Statements

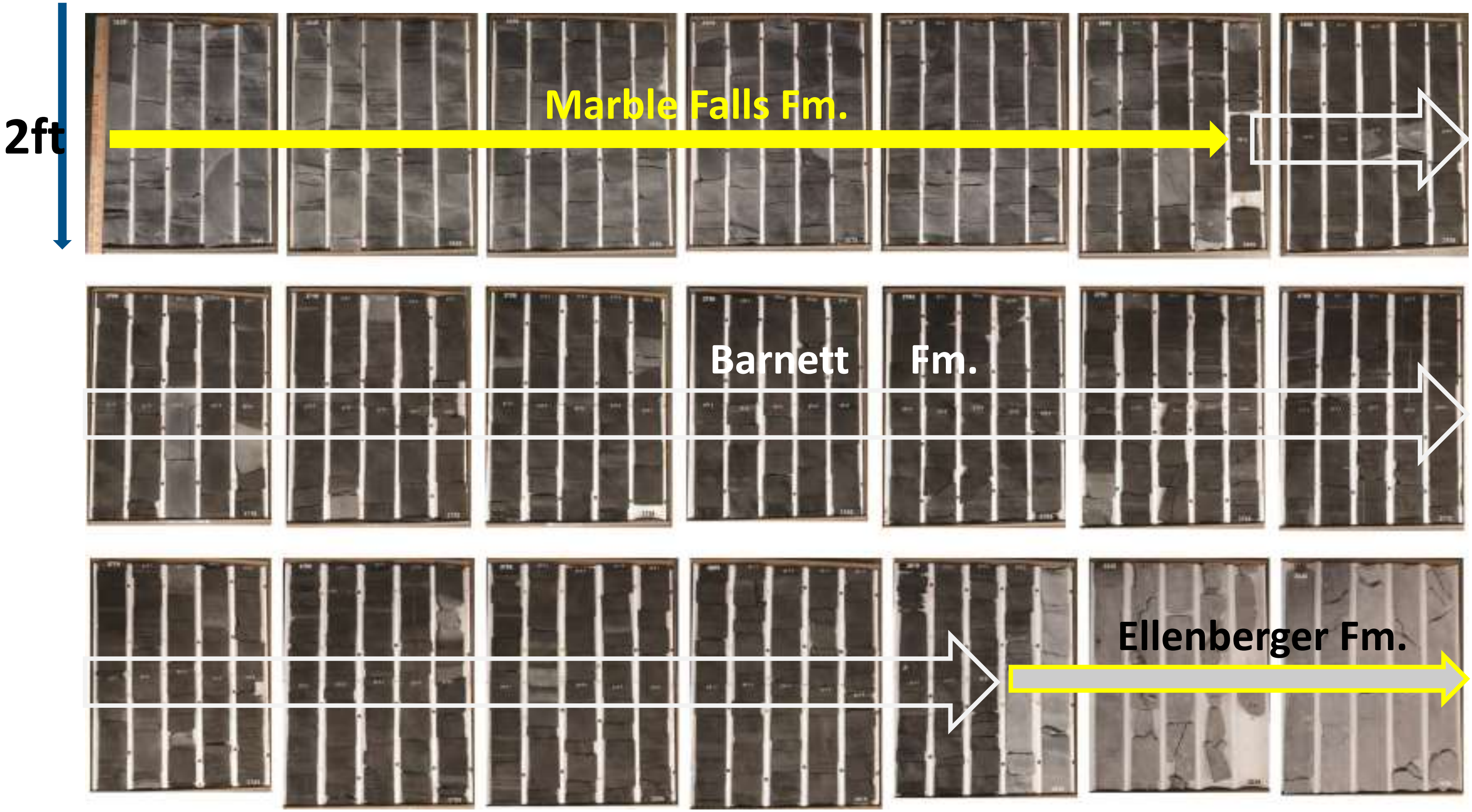
- **A mudrock stratigraphy is more useful with a geochemical/mineralogical context.**
  - **Why? Because of the fine-grained and *seemingly* invariant nature of many mudrock successions.**
  - **Because different people call the same rock something different…lack of consensus and quantification.**

- **One's ability to quantify chemostratigraphic changes takes about as long as undertaking qualitative work—let's try to avoid "soft geochemistry".**
  - **How? Through careful calibration of XRF spectra (using real mudrocks as references, not x-ray theory): *Why be qualitative, when you can be quantitative?***

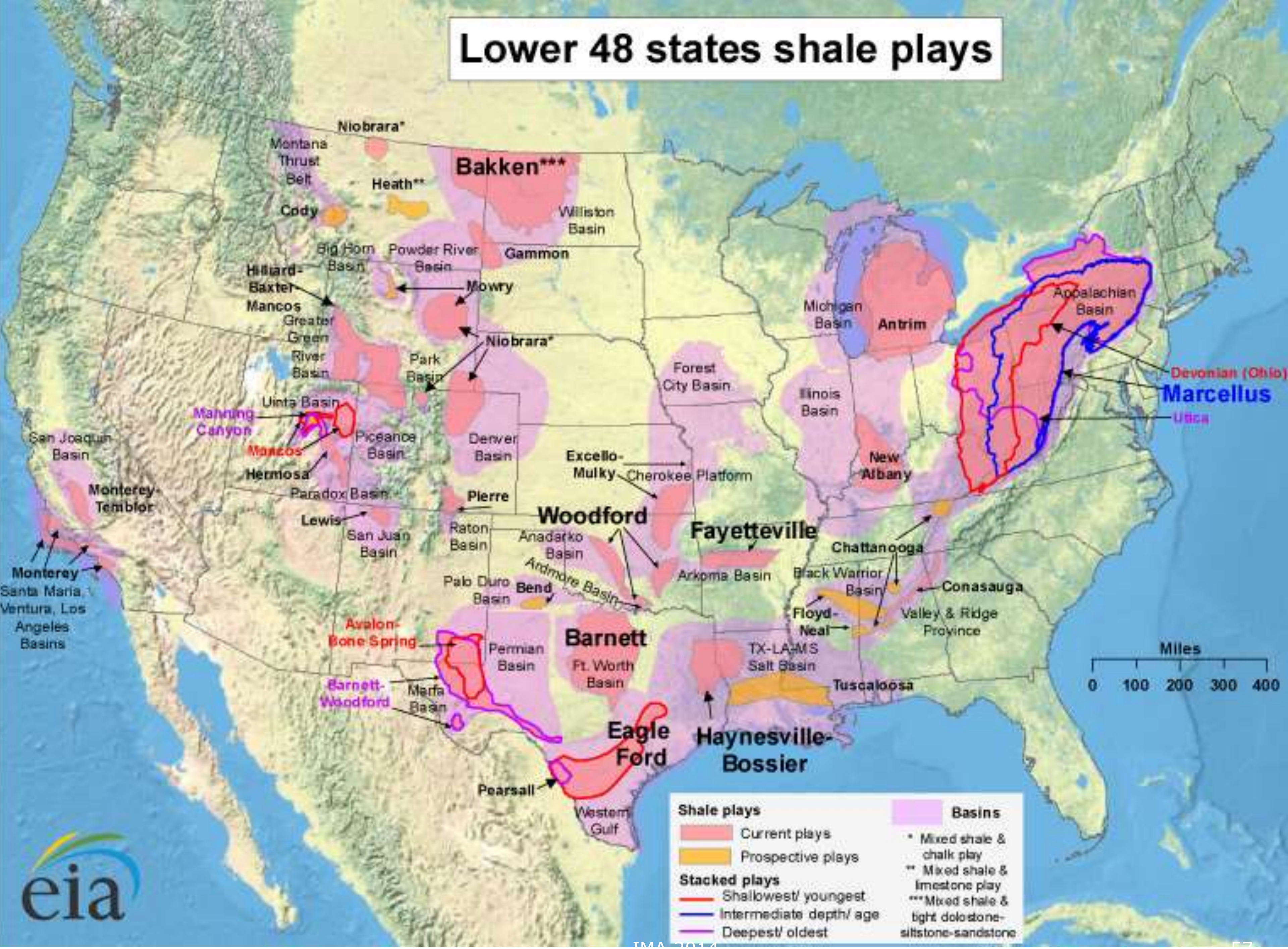
- **Just because you get an elemental "answer" does not signify that the element is *measurable*, and it certainly does not indicate that the answer is *correct*.**
  - **Why not? Because those who design the instrument and software are focused on just that---the instrument and the software—not the elemental abundance and distribution in your geological materials.**

Chemostratigraphy

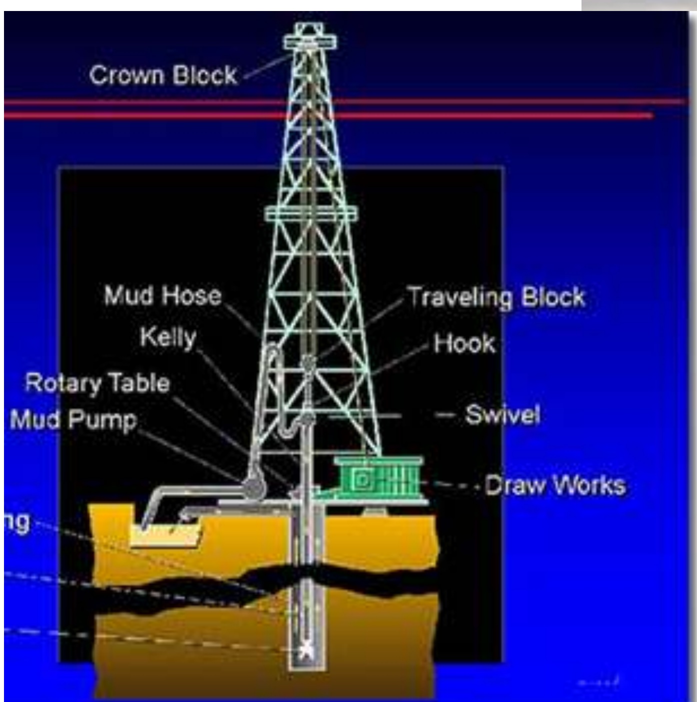
a rapid method for generating chemical data in drill cores.



NOTE: Any one box of Barnett Shale looks almost exactly like the other boxes….

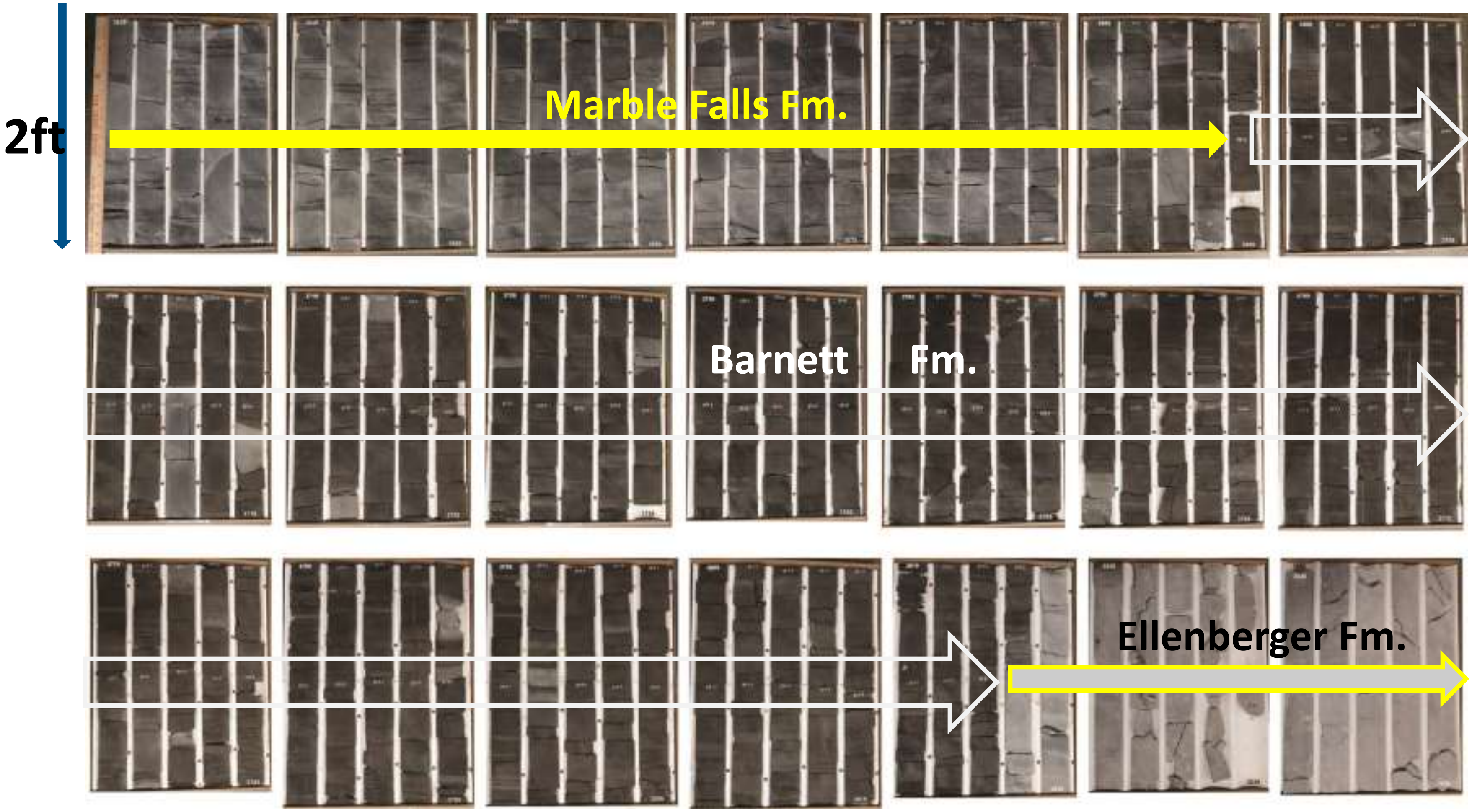

Lower 48 states shale plays
Niobrara*
Montana Thrust Belt
Bakken***
Heath**
Cody
Williston Basin
Big Horn Basin
Powder River Basin
Gammon
Hilliard-Baxter-Mancos
Mowry
Greater Green River Basin
Niobrara*
Park Basin
Uinta Basin
Manning Canyon
Mancos
Hermosa
Piceance Basin
Denver Basin
Paradox Basin
Lewis
San Juan Basin
Pierre
Raton Basin
San Joaquin Basin
Monterey-Temblor
Monterey
Santa Maria, Ventura, Los Angeles Basins
Forest City Basin
Excello-Mulky
Cherokee Platform
Woodford
Anadarko Basin
Ardmore Basin
Fayetteville
Arkoma Basin
Palo Duro Basin
Bend
Avalon-Bone Spring
Permian Basin
Barnett
Ft. Worth Basin
Barnett-Woodford
Marfa Basin
Eagle Ford
Pearsall
Western Gulf
Haynesville-Bossier
TX-LA-MS Salt Basin
Tuscaloosa
Michigan Basin
Antrim
Illinois Basin
New Albany
Black Warrior Basin
Chattanooga
Conasauga
Floyd-Neal
Valley & Ridge Province
Appalachian Basin
Devonian (Ohio)
Marcellus
Utica
Miles
0 100 200 300 400
Shale plays
Current plays
Prospective plays
Stacked plays
Shallowest/ youngest
Intermediate depth/ age
Deepest/ oldest
Basins
* Mixed shale & chalk play
** Mixed shale & limestone play
*** Mixed shale & tight dolostone-siltstone-sandstone
eia

XRF on Drill rig....




Regina
Winnipeg
Bakken
Bismarck
Fargo
Duluth
Rapid City
Minneapolis
St. Paul
Austin
San Antonio
Eagle Ford Shale

Mudrock cores….



NOTE: Any one box of Barnett Shale looks almost exactly like the other boxes….

MUDROCK DRILL CUTTINGS

Most XRF work in O&G is done out in the field, on a drill rig, using drill cuttings; core is a luxury.

The Application documented for all!

Chemical Geology 324–325 (2012) 122–131

Contents lists available at SciVerse ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Research paper

The quantification and application of handheld energy-dispersive x-ray fluorescence (ED-XRF) in mudrock chemostratigraphy and geochemistry

Harry Rowe, Niki Hughes *, Krystin Robinson

Earth and Environmental Sciences, University of Texas at Arlington, 500 Yates Street, Arlington, TX, USA

Reference Materials

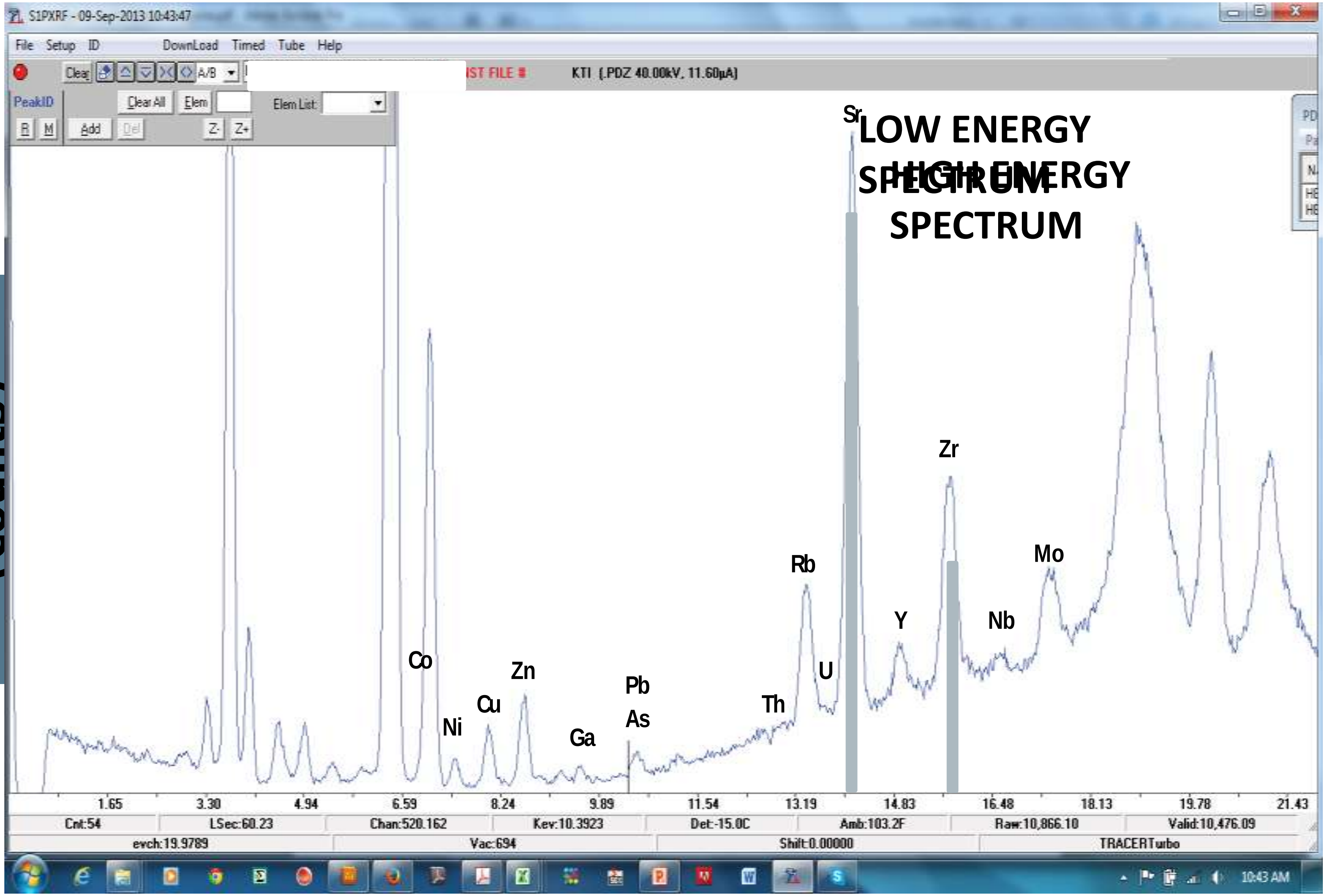
- **Originally selected *starting* reference materials by scanning cores and picking peaks that reflected high/low/medium elemental concentrations**
- **Had references analyzed by WD-XRF of fused pellet and ICP-MS analysis of borate fusion at SGS (Canada)**
- **Reference powders pressed into pellets (40-ton press)**
- **Pressed with boric acid backing**

Sample Selection

Table 1
Tally of minimum and maximum elemental concentrations for the suite of calibration standards and in-house reference materials.

Standards and reference materials												
	Standards[a]		Woodford Fm.[b]		Ohio Shale[c]		Barnett Fm.[d]		Smithwick Fm.[e]		Eagle Ford Fm.[f]	
n[g]	5		27		7		16		20		15	
Element	Range of values for each formation											
	Min[h]	Max[h]	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Mg (%)	0.93	4.89	0.27	**10.25**	0.66	1.08	0.52	2.64	0.63	1.88	**0.24**	0.66
Al (%)	3.45	9.96	**0.64**	7.62	6.87	10.77	1.20	8.47	1.00	**13.07**	1.07	5.98
Si (%)	13.2	29.3	5.89	**38.2**	26.8	28.8	6.22	32.7	8.79	34.8	**3.75**	22.6
P (%)	0.02	0.14	**0.01**	0.48	0.02	0.17	0.07	**0.98**	0.03	0.12	0.02	0.15
S (%)	0.01	5.35	0.46	5.32	0.72	2.25	0.25	2.24	0.02	2.00	0.33	3.81
K (%)	1.15	3.45	0.17	3.51	2.92	**4.32**	0.27	1.83	0.22	3.12	**0.14**	1.61
Ca (%)	0.43	5.99	**0.07**	18.1	0.19	0.71	2.77	31.2	0.32	27.7	9.36	**34.7**
Ti (%)	0.16	0.43	**0.04**	0.33	0.40	0.53	0.07	0.46	0.05	**0.53**	0.04	0.39
Mn (%)	0.015	0.046	**0.008**	**0.325**	0.008	0.031	0.008	0.031	0.008	0.147	0.008	0.023
Fe (%)	2.12	**6.53**	0.61	4.92	3.09	4.60	0.64	3.54	1.66	6.38	**0.43**	3.57
Ba (ppm)	290	820	842	5750	434.3	562	63.5	625	357	**9050**	**30.3**	295
V (ppm)	87	160	51	**1720**	141	385.5	**22**	165	24	196	41	899
Cr (ppm)	30	123	20	260	62	96	40	**295**	40	120	**10**	100
Ni (ppm)	27	122	17	**302**	33.5	136.8	26	168	22	144	**11**	155
Cu (ppm)	28.7	66	8	**485**	22.3	60.5	12	83.5	8	54	**5**	66
Zn (ppm)	55	103	24	**1220**	77.1	505.3	57	387	45	301	**20**	503
Th (ppm)	4.8	12.8	**1.3**	10.7	9.1	14	2	12.9	2.1	**14.6**	1.6	9.9
Rb (ppm)	59	205	13.9	200	140.8	**224.1**	16.5	121	15.3	167	**6.4**	91.7
U (ppm)	1.5	48.8	3.36	**66**	7.2	37.3	**1.22**	11.4	1.81	6.62	1.67	14
Sr (ppm)	54	420	**36.4**	483	105.3	145	248	**869**	107	518	329	791
Y (ppm)	13	40.6	**5.8**	52.7	26.2	37.2	10.9	**62**	20	35.3	7.6	22.3
Zr (ppm)	53	165	**15.5**	122	133.9	217.7	25	146	17.2	**338**	32.6	215
Nb (ppm)	5.2	14.3	**2**	13	14	16	2	15	2	15	3	**22**
Mo (ppm)	1.4	134	9	**166**	**1.3**	153.7	2	13	2	3	3	95
Total min/max[i]	0	1	10	9	1	2	2	4	0	5	10	2

Data Acquisition: Qualitative Real-Time Spectra



Intensity (counts)

Energy in Kev

Some more exciting tables…

Table 3
Accepted versus measured elemental concentrations, inter-pellet standard deviations, intra-pellet standard deviation, and limits of determination of a method for one internationally accepted standard (SARM-41), and one in-house reference material (RTC-W-220) prepared using pulverized sample from the Mississippian-age Woodford Formation.

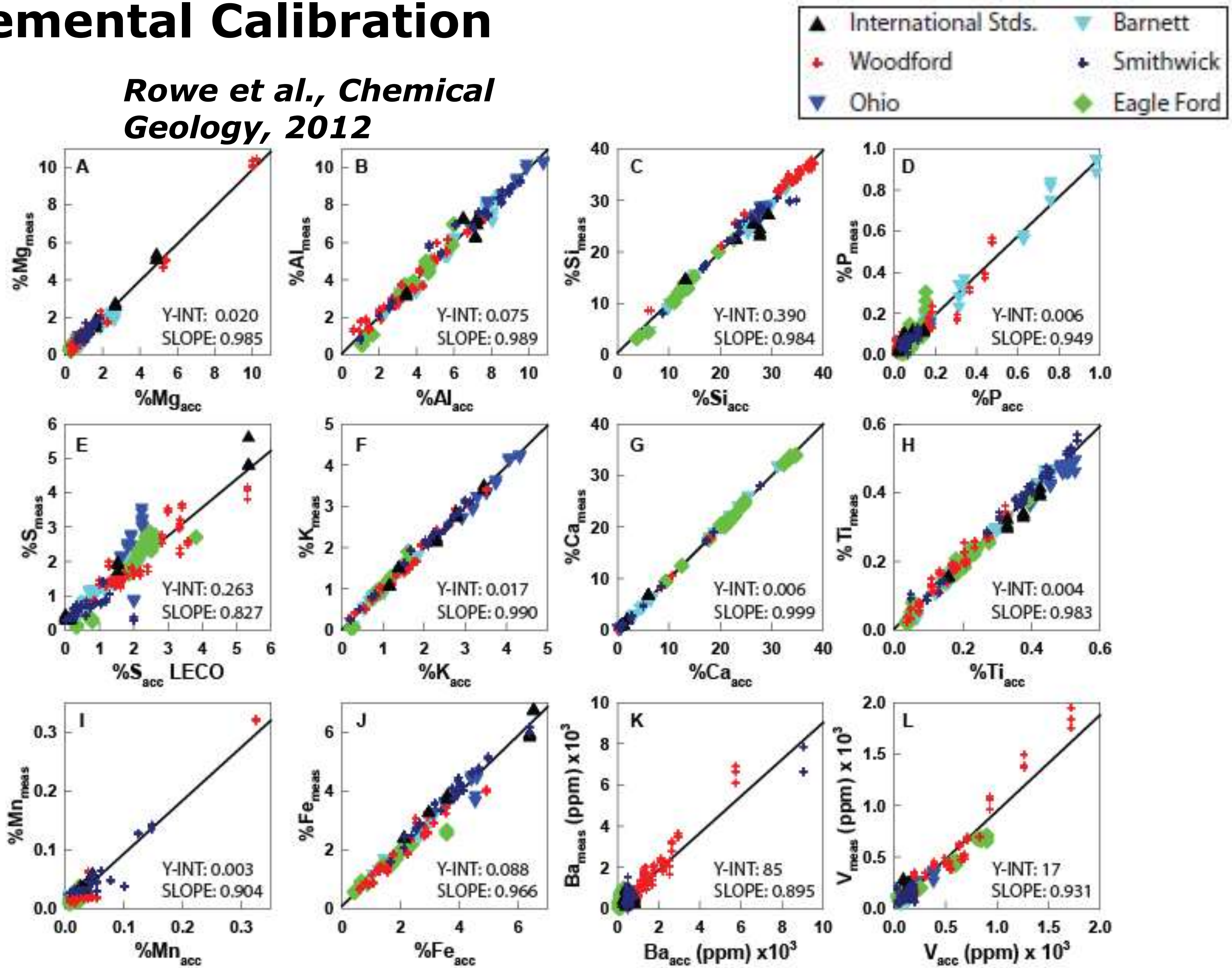
Element	SARM-41					RTC-W-220 (Woodford Fm.)				
	Accepted value[a]	Measured value[b]	$\sigma_{7\,pellets}$[c]	$\sigma_{1\,pellet}$[d]	LDM[e]	Accepted value[a]	Measured value[b]	$\sigma_{7\,pellets}$[c]	$\sigma_{1\,pellet}$[d]	LDM[e]
Mg (%)	4.9	5.0	0.17	0.20	0.33	0.67	0.80	0.09	0.17	0.17
Al (%)	7.14	5.89	0.14	0.10	0.28	4.96	5.39	0.14	0.05	0.28
Si (%)	26.5	24.0	0.2	0.2	0.5	32.6	33.7	0.2	0.2	0.5
P (%)	0.02	0.02	0.02	0.01	0.03	0.07	0.05	0.03	0.03	0.07
S (%)	0.15	0.19	0.02	0.01	0.04	3.34	2.18	0.10	0.04	0.20
K (%)	1.15	1.02	0.02	0.02	0.04	2.07	2.31	0.09	0.04	0.18
Ca (%)	1.07	0.99	0.03	0.01	0.06	0.13	0.23	0.03	0.00	0.06
Ti (%)	0.33	0.29	0.01	0.02	0.02	0.23	0.27	0.02	0.01	0.04
Mn (%)	0.046	0.056	0.003	0.002	0.006	0.015	0.012	0.001	0.001	0.002
Fe (%)	2.96	3.20	0.03	0.01	0.06	2.93	2.55	0.06	0.02	0.12
Ba (ppm)	820	802	214	147	428	2090	1884	376	83	753
V (ppm)	139	167	41	44	82	928	1114	68	66	137
Cr (ppm)	123	106	16	9	32	110	98	13	9	26
Ni (ppm)	122	79	17	8	34	130	153	26	20	52
Cu (ppm)	53	65	24	14	48	83	147	20	16	40
Zn (ppm)	76	67	7	11	14	823	844	96	30	191
Th (ppm)	12	7	1	1	2	8.4	9	1	2	2
Rb (ppm)	59	45	3	3	6	122	123	12	4	25
U (ppm)	2	3	2	3	4	18.1	17	6	4	11
Sr (ppm)	54	47	2	1	4	75.5	87	5	4	10
Y (ppm)	17	17	1	1	3	35.4	34	3	2	5
Zr (ppm)	146	130	5	4	11	80.3	95	7	2	13

U, La1	Rh	Rb, U, Sr	20[b]
Sr, Ka1	Ca, Mn, Rb, Sr, Rh	U, Sr	5
Y, Ka1	Th, Rh	Rb, Y	4
Zr, Ka1	Y, Zr, Rh	Sr, Zr	4
Nb, Ka1	Rh	Y, Zr, Nb, Mo	3
Mo, Ka1	Ti	Zr, Nb, Mo	70[b]

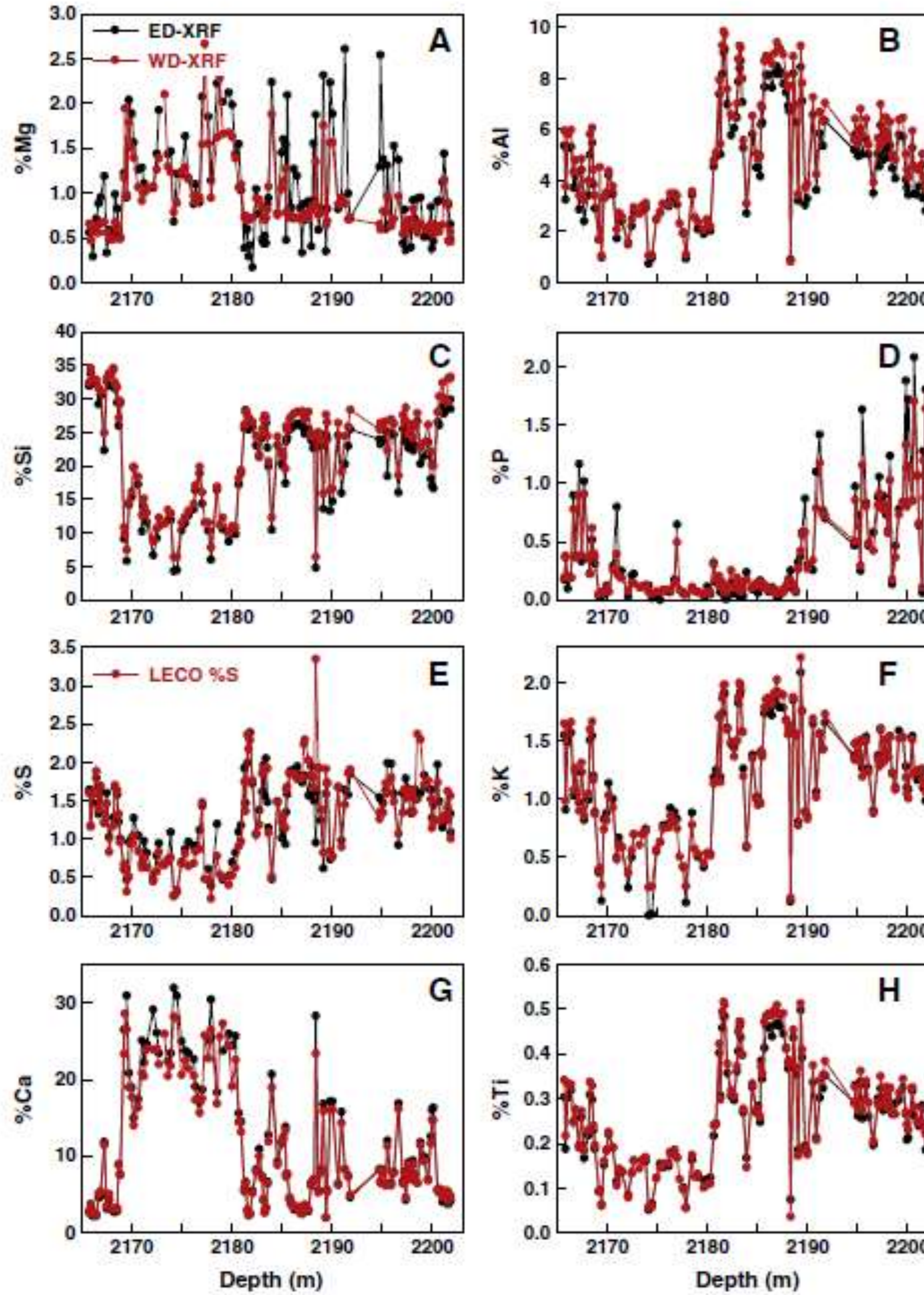
Limit of Determination of a Method (Rousseau, 2001)

Elemental Calibration

Rowe et al., Chemical Geology, 2012



Comparison HH vs. WD-XRF



Why did this approach work so well?

- **Mudrocks are already very homogeneous at a very small scale.**
- **The average grain size in a mudrock is on the order of 5 microns.**
- **Pulverizing the sample only serves to help the already homogeneous sample.**

Why didn't it work better?

- **Some pressed pellets were not thick enough…listen next time.**
- **Some references were not pulverized enough…listen next time.**
- **We created error by scanning each reference pellet 3 times and moving it around on the nose of the instrument between measurements…not necessary, but a good waste of time.**

Onto the next version with improved performance!

Harry Rowe

Bureau of Economic Geology

University of Texas at Austin

“Manual” HH-ED-XRF Workflow

- Wash
- Label
- Scan
- Drill
- Rinse
- Repeat

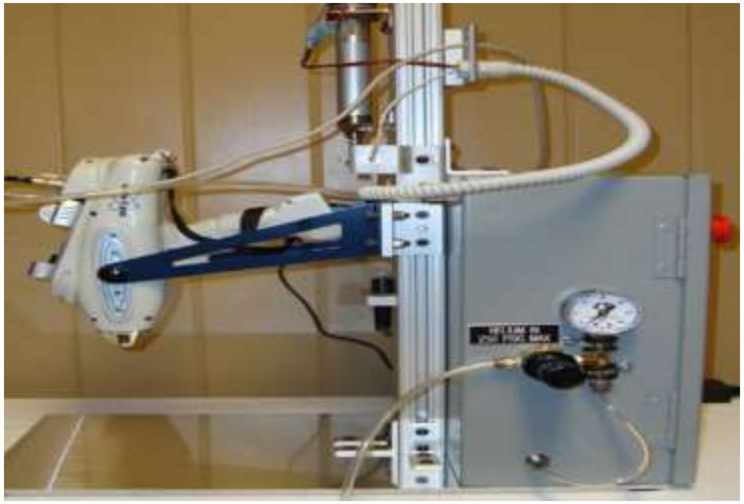
Core Scanner attachment with Camera and full quantification support for TRACER

Max 4 inch core in 3 feet (1 m) standard segments
TRACER IV SD system with He purge for Na-U elemental range

Core Scanner accessory for TRACER

1 m core

TRACER Series Instrument for the most flexible use …



S1 TRACER III Series and IV Series

HandHeld
Portable
Benchtop
Desktop

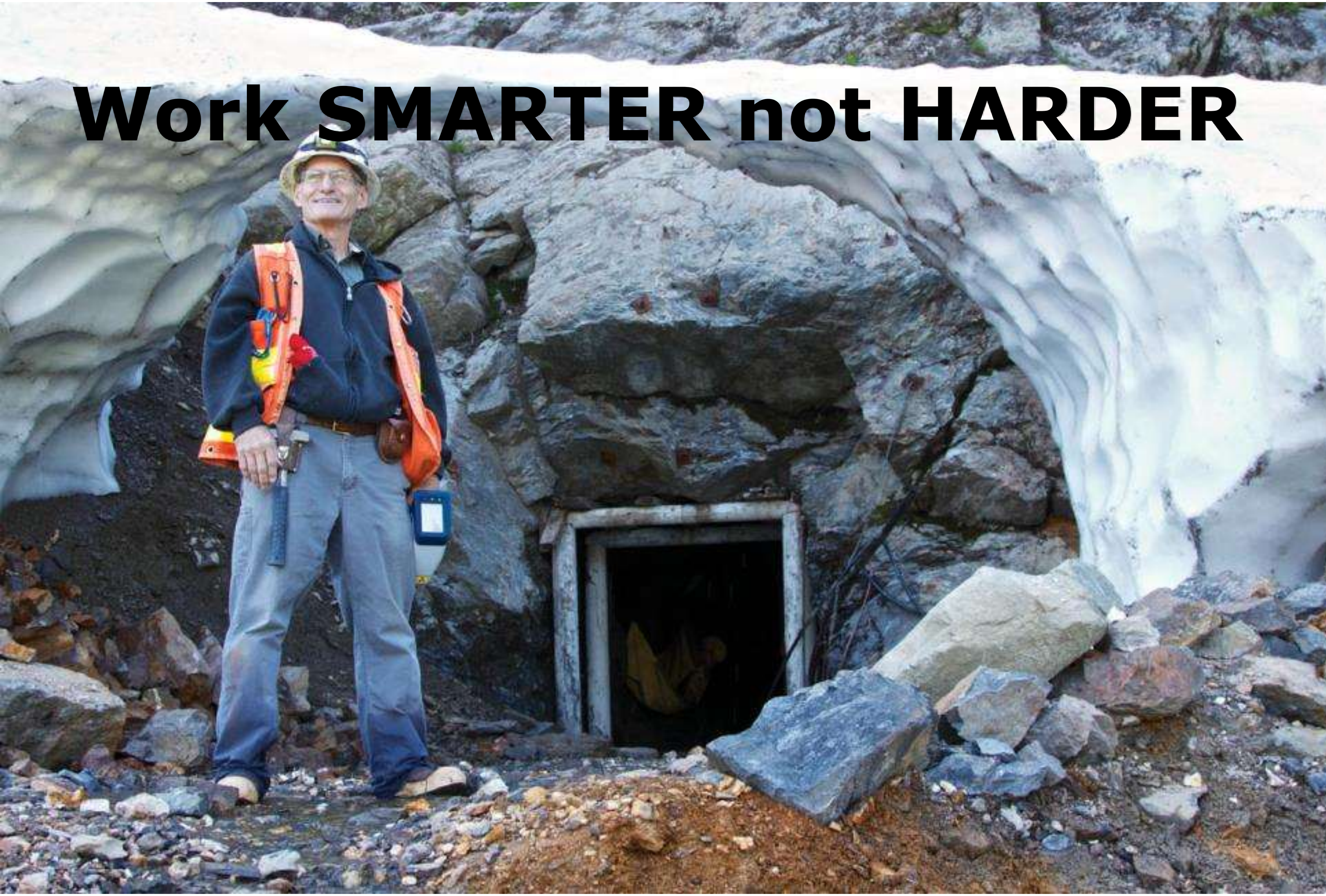
The ONLY
Crossover

SPECTROMETER
With all SW for
CUSTOM
CALIBRATION

CONCLUSION

- Good data can be achieved with the right pXRF/ HH XRF approach
- Generic calibrations (vendor provided) can be used for screening and semi-quantitative analysis provided that sample and calibration approach fit
- “Tuned” or type standardized calibration (based on the vendor application) using some matrix matched reference samples are useful and required if the samples are not “apples to apples” and higher accuracy is required
- For publication and data comparison between units it is recommended to modify the base calibration using matrix matched samples or create a dedicated calibration
- BRUKER Instruments can “switch” calibrations enabling to automatically select the “right” one ….

Work SMARTER not HARDER



How to learn more and get hands on experience

- Free BRUKER HH XRF Workshops :
  - http://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/handheld-xrf/workshop/workshop-overview.html
- SME/GSA Meeting Workshops
- U Texas (Dallas) MUDROCK training
- UWO Ontario, Canada Seminars
- WSU Washington USA Seminars

The University of Western Ontario

Department of Earth Sciences

X-RAY FLUORESCENCE SPECTROMETRY

short course with special topical workshops

June 2 – June 13 , 2014

Week I - Fundamentals, Instrumentation and QA/QC of Methods

Week II - Quantitative Analysis, Methods Development and Data Reduction Methods

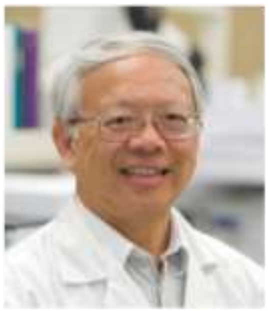
Special Topical Workshops –

June 6, Sample Preparation for XRF Analysis

For more information
http://www.uwo.ca/earth/xrfcourse

The University of Western Ontario

Department of Earth Sciences



Dr. Charles Wu

University of Western Ontario
Senior Research Scientist, BIOTRON Research Centre

Organizer and Lecturer, UWO XRF Short Course

ctwu@uwo.ca

Alexander Seyfarth

Bruker Elemental
Sr. Product Manager HHXRF
Lecturer, UWO XRF Short Course
alexander.seyfarth@bruker-elemental.net

Department of Earth Sciences
University of Western Ontario

Biology & Geological Sciences Bldg.,
University of Western Ontario
London, Ontario, CANADA N6A 5B7
Phone: 519-661-3187
Fax: 519-850-2573

www.bruker.com

Literature citations on pXRF

- Glanzman, Kloos in "Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration" edited by B. Milkereit, 2007, p. 291-301

- Taylor, P.D, Ramsey, M.H. and Potts, P.J., 2004, Balancing Measurement Uncertainty against Financial Benefits: Comparison of In Situ and Ex Situ Analysis of Contaminated Land: Environ. Sci. & Tech., 38, 6824-6831.

- Potts PJ, West M (2008) Portable X-ray Fluorescence Spectrometry: Capabilities for In Situ Analysis. RSC publishing, London, UK, 291 pp

2014 S1 TITAN 200,300, 600,800

S1 TITAN MODELS

S1TITAN Configurations	Excitation	Detector	Elemental Range	Spot Size	Calibrations									
					Alloy	Alloy LE	Precious Metals	Low Lead in Copper	Restricted Materials	Regulated Metals	Regulated Plastics	Limestone	GeoChem	Soil
Model 800	6-50kV 4 filters	FAST SDD™	Mg - U	8, 5 or 3*mm		●	●	●	●			●	●	●
Model 600	15-50kV 4 filters	FAST SDD™	Mg - U	5mm		●	●	●	●			●	●	●
Model 300	15-50kV 4 filters	SiPIN	Cl - U	5mm	●		●			●	●		●	●
Model 200	45kV Fixed filter	SiPIN	Ti - U	5mm	●		●							

S1 TRACER III Series and IV Series 2008-….

Benchtop
Desktop
Crossover
Point&Shoot

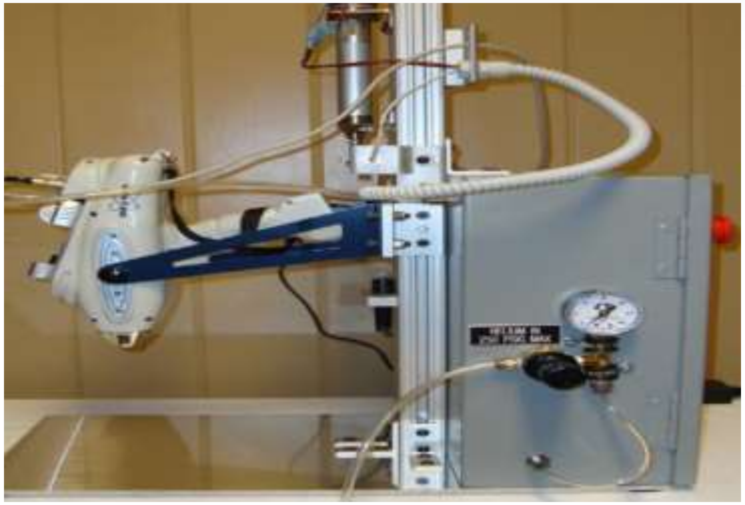
SPECTROMETER
With all SW for
CUSTOM CALIBRATION

RSC-20 LAB FEATURES

- LAB VERSION includes shipping crate and 1 TRAY
- FIELD VERSION includes shipping crate + PELCICAN CASE and 1 TRAY
- AVAILABLE TRAYS are

XSC-001	Rotary Table for Sample Cups	Removable 20-position Table Assembly for use with the Rotary XRF Sample Changer. Accommodates standard Chemplex® 1940 XRF Sample Cups. Manufactured using stable plate materials and precision machining techniques required to maintain a flat table.
XSC-008	Rotary Table for Sample Cups	Removable 20-position Table Assembly for use with the Rotary XRF Sample Changer. Accommodates standard Accommodates Premier SC-4231 XRF Sample Cups (OD 32mm). Manufactured using stable plate materials and precision machining techniques required to maintain a flat table.
XSC-002	Rotary Table for Loose Samples	Removable 20-position Table Assembly for use with the Rotary XRF Sample Changer. Accommodates loose samples. Manufactured using stable plate materials and precision machining techniques required to maintain a flat table.

TRACER BT SAMPLE CHANGER WITH HE MMS 300H



- Rugged Industrial Design
- Up to 12Inch sample height
- Helium Shield Gas Management

Core Scanner attachment with Camera and full quantification support for TRACER

Max 4 inch core in 3 feet (1 m) standard segments
TRACER IV SD system with He purge for Na-U elemental range

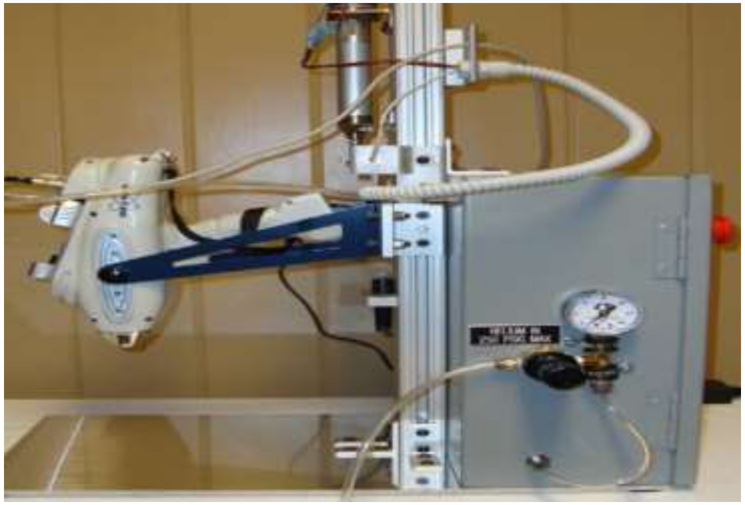
NON PRICE LIST ITEM: Please ask your RSM for pricing and availability

Core Scanner accessory for TRACER

NON PRICE LIST ITEM: Please ask your RSM for pricing and availability

SNEAK PEAK
NEW “SAMPLE CHANGER” for tube on top setup to minimize cross contamination

TRACER BT SAMPLE CHANGER WITH HE MMS 300H



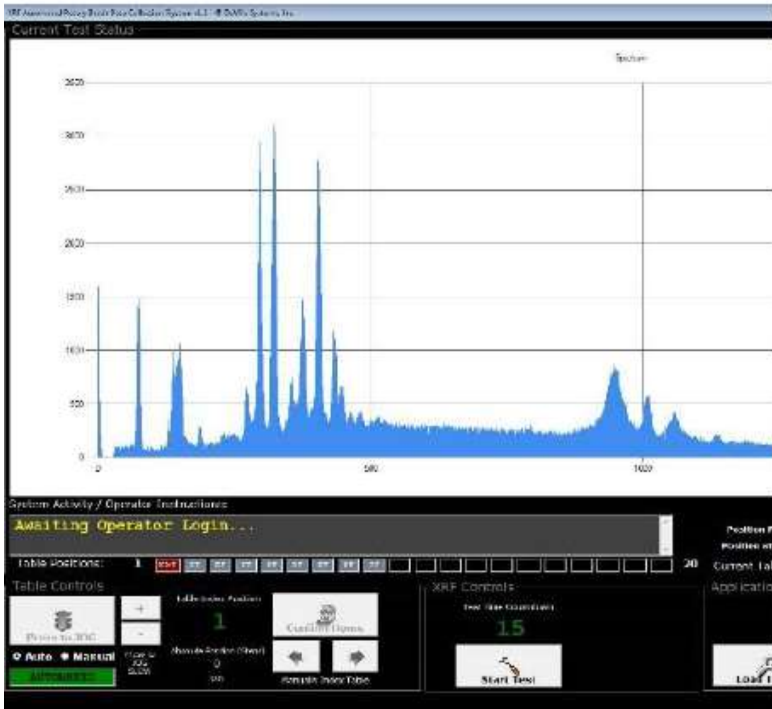
- Rugged Industrial Design
- Up to 12Inch sample height
- Helium Shield Gas Management

SNEAK PEAK
NEW “SAMPLE CHANGER” for tube on top setup to minimize cross contamination

BENCHTOP STAND WITH SAMPLE CHANGER (LAB)

- DE WITT RSC -2- FOR BRUKER TRACER models

RSC-20 FEATURES

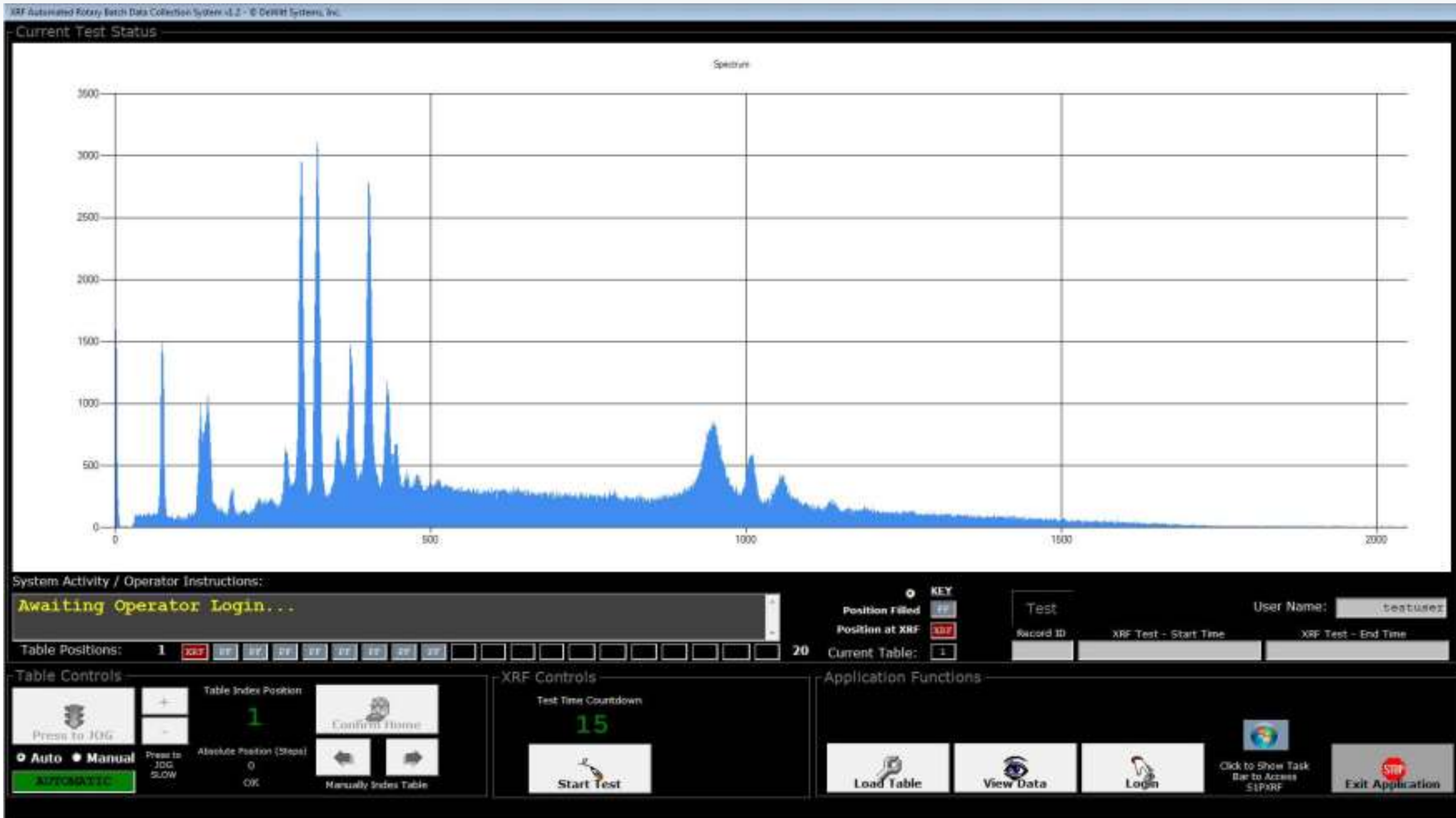


RSC-20 Features

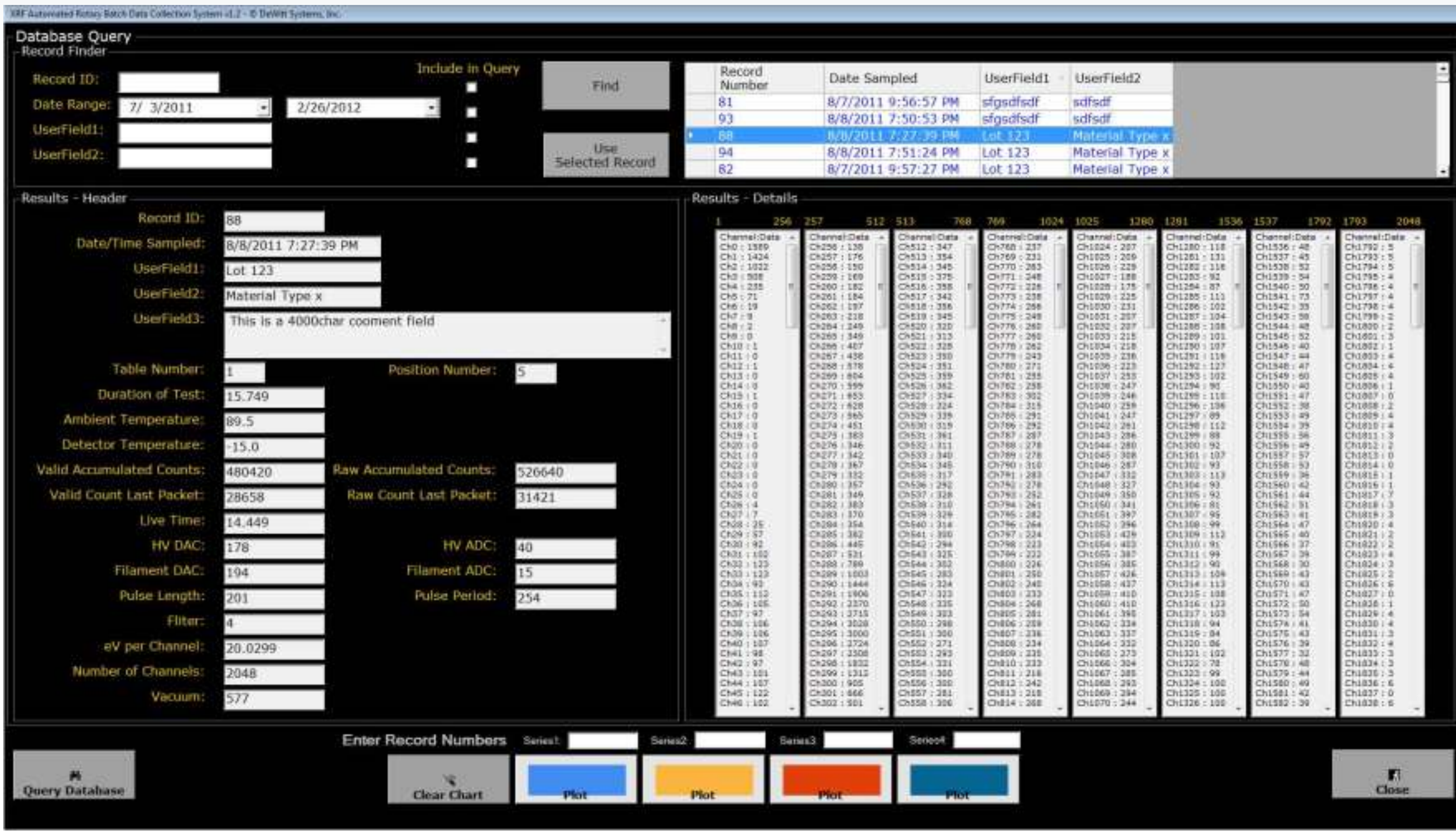
- Designed for High Reliability with Heavy Duty Construction
- Supports standard sample cups and loose samples
- Automation Control System with Universal Power Supply
- Stores operator-supplied SAMPLE ID data with association to RAW spectra collected by the XRF Instrument into a standard SQL Database
- Standard software includes tools to perform comparative data plotting and raw data record search and display.
- Available Travel Kit Version FIELD VERSION
- Custom Tables available to meet specific customer applications
- 1 year system warranty with option to extend

- LAB and FIELD VERSION
- INCLUDES CONTROL SW AND PC

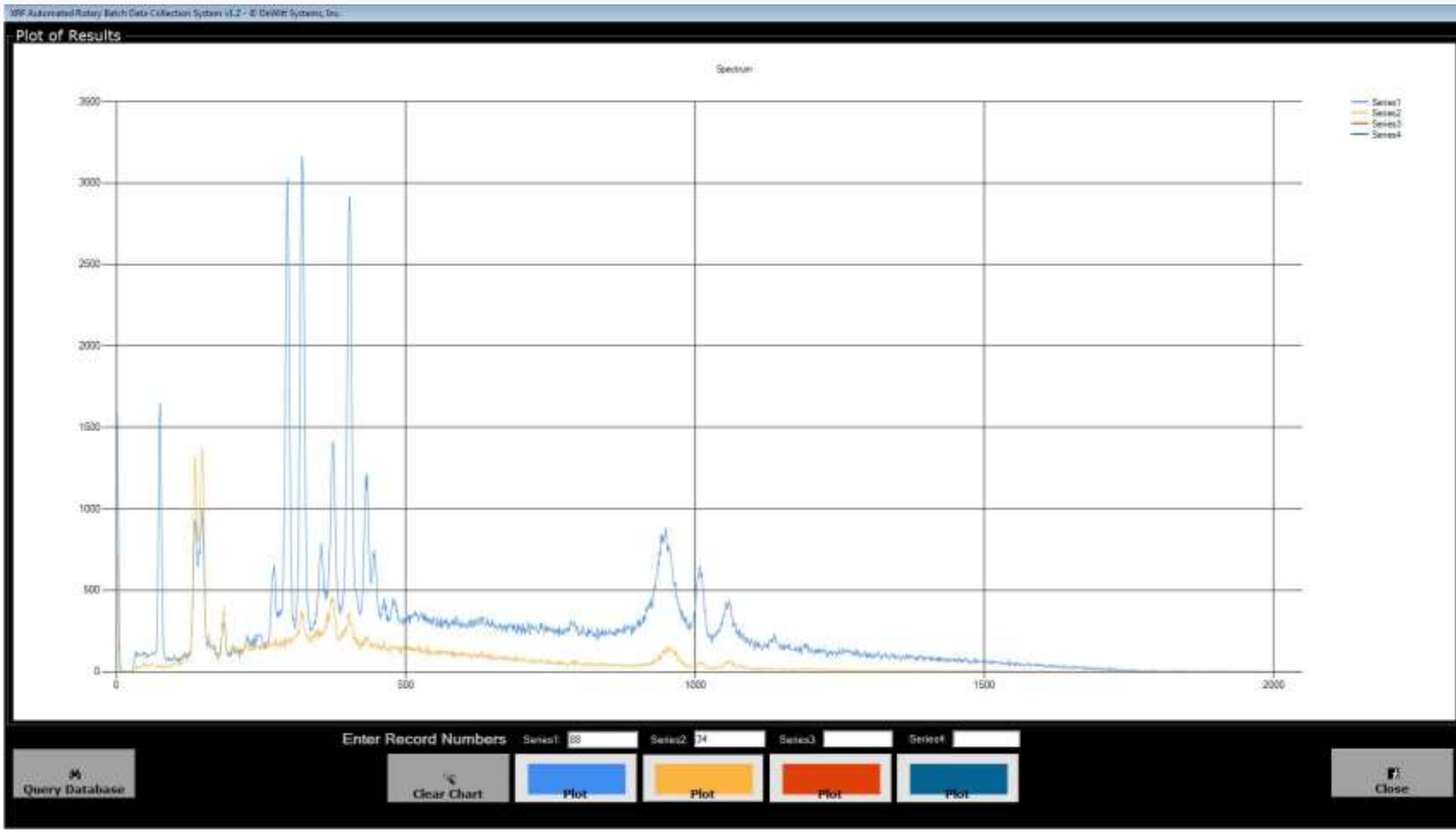
RSC-20 FEATURES



RSC-20 FEATURES



RSC-20 FEATURES



RSC-20 FEATURES details