NABIR Field Research Center
Oak Ridge, Tennessee

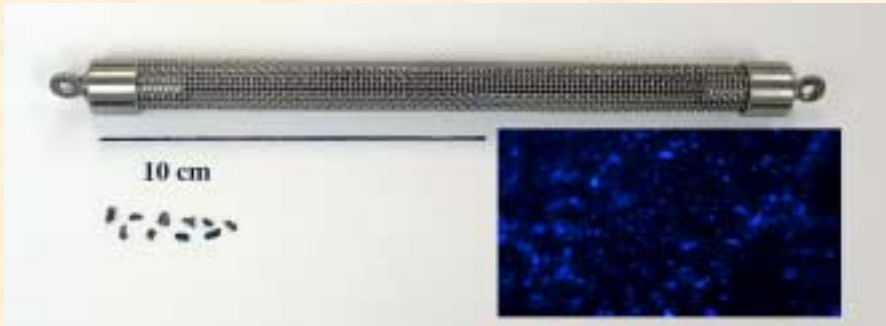
Update on Site Characterization
September 23, 2003 FRC Workshop

David Watson (865-241-4749) - FRC Manager
Environmental Sciences Division
Oak Ridge National Laboratory
E-Mail: watsondb@ornl.gov

http://www.esd.ornl.gov/nabirfrc/

Characterization Update

- **Area 2 characterization**
- **Mineralogical and geochemical evaluations**
  - **Area 2 core**
  - **Area 3 rotasonic cores**
- **Geophysics Evaluations**
  - **Electromagnetic borehole profiling – ORNL**
  - **Seismic and Radar - LBNL**
  - **Geoprobe conductivity probing**
  - **Gamma counting - Thorium 232 finding**
- **Humics – Background Area forested surface soils**
  - **Spectroscopic characterization (Baohua Gu)**
- **Coupons – Microbial analysis INEL and UT**

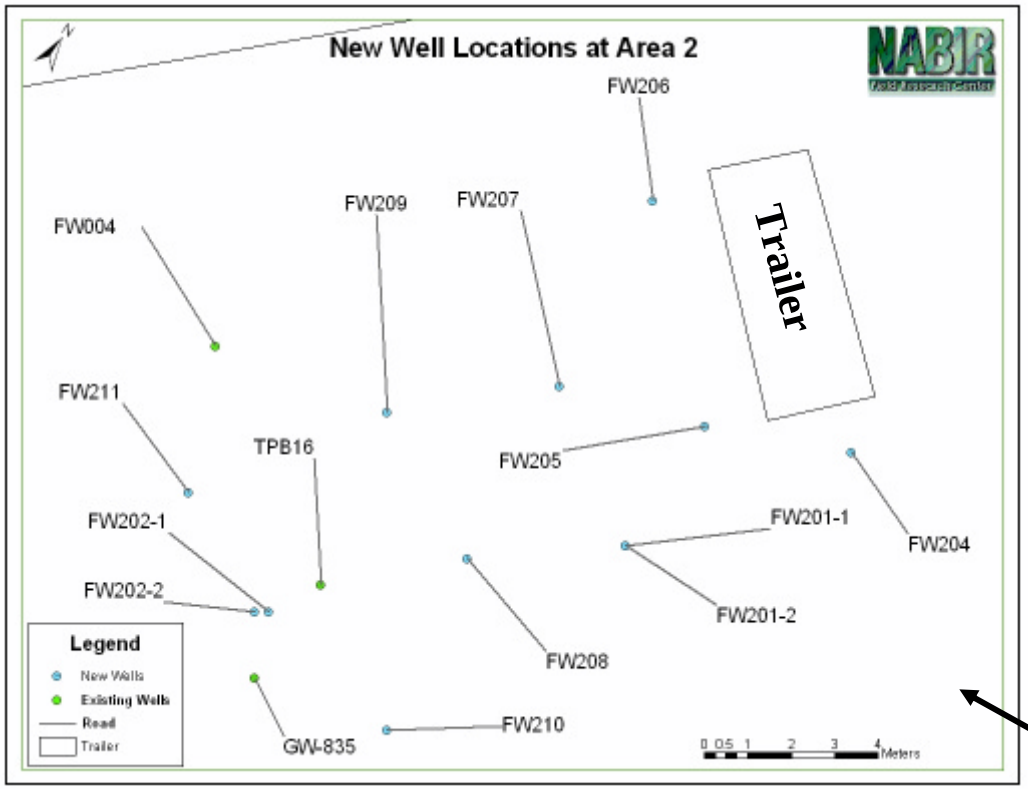


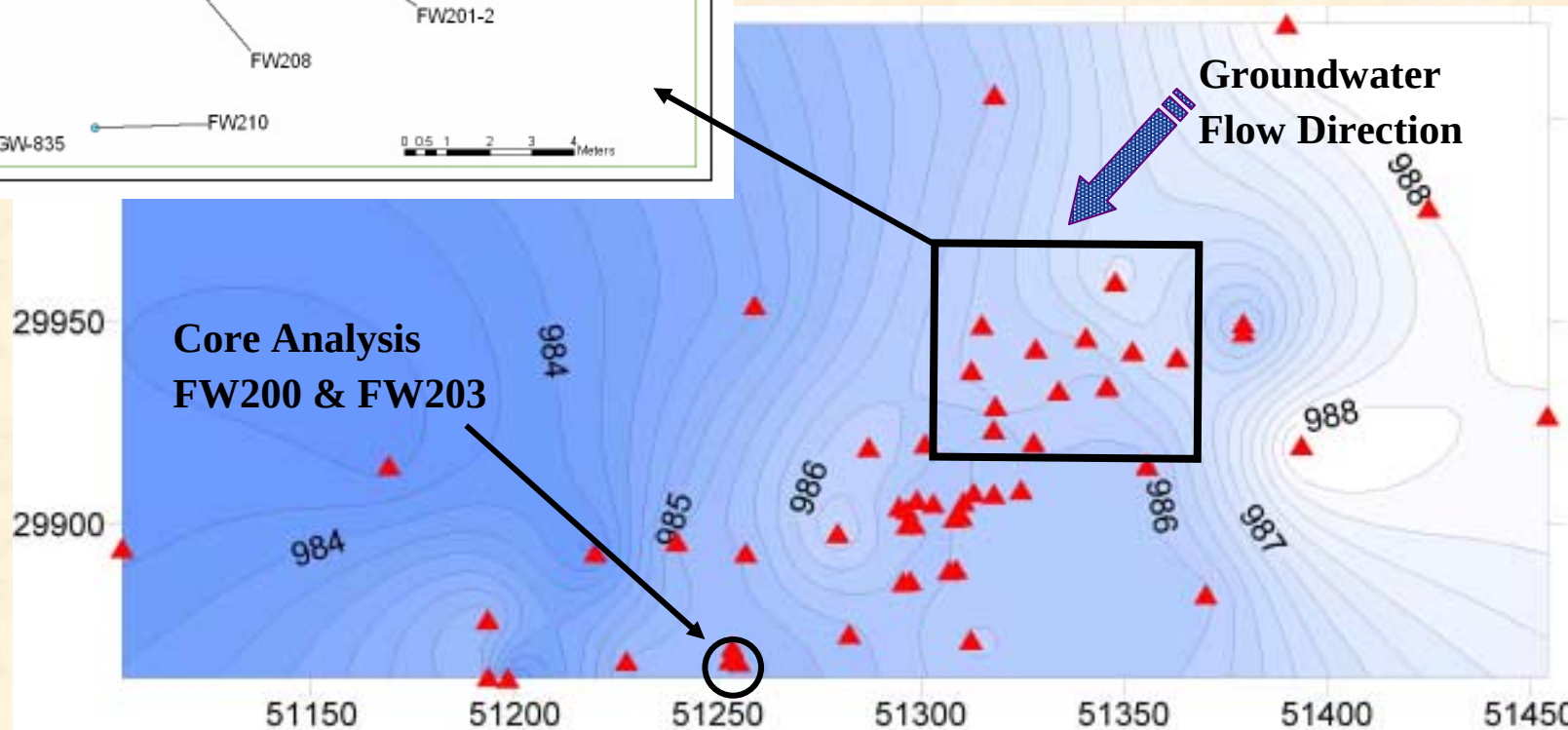
Area 2 Site Characterization

- **12 new wells installed (2 multiports)**
- **Groundwater sampling**
  - **Cations (ICP/MS)**
  - **Anions (IC)**
  - **TOC**
  - **Field Parameters**
- **Water levels**
- **Coring with mineralogical and geochemical analysis - Roh**
  - **McKinley and Roden also conducting core analysis**

Area 2
Location of new wells

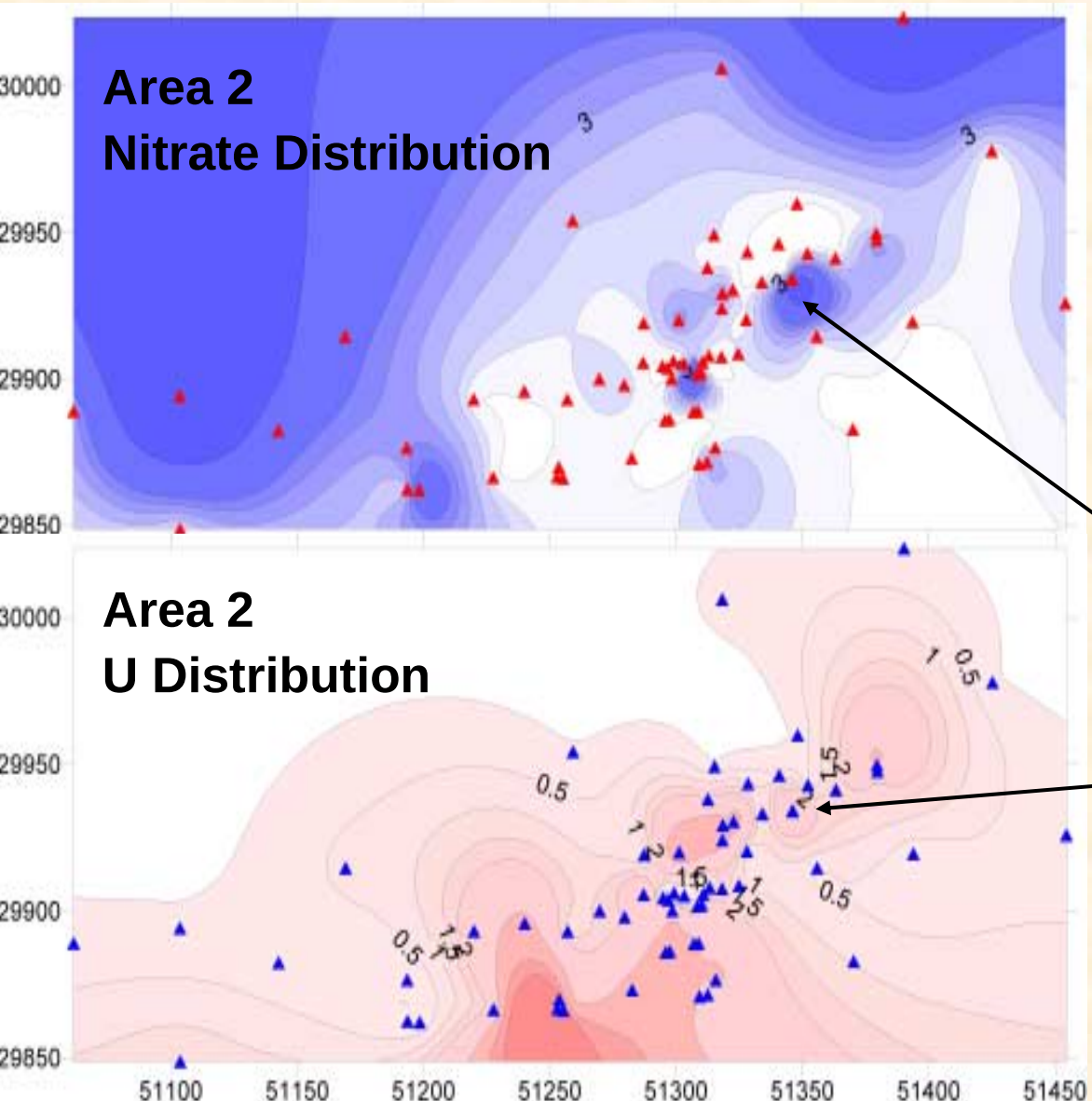
- **OSU project**
- **PNNL project**

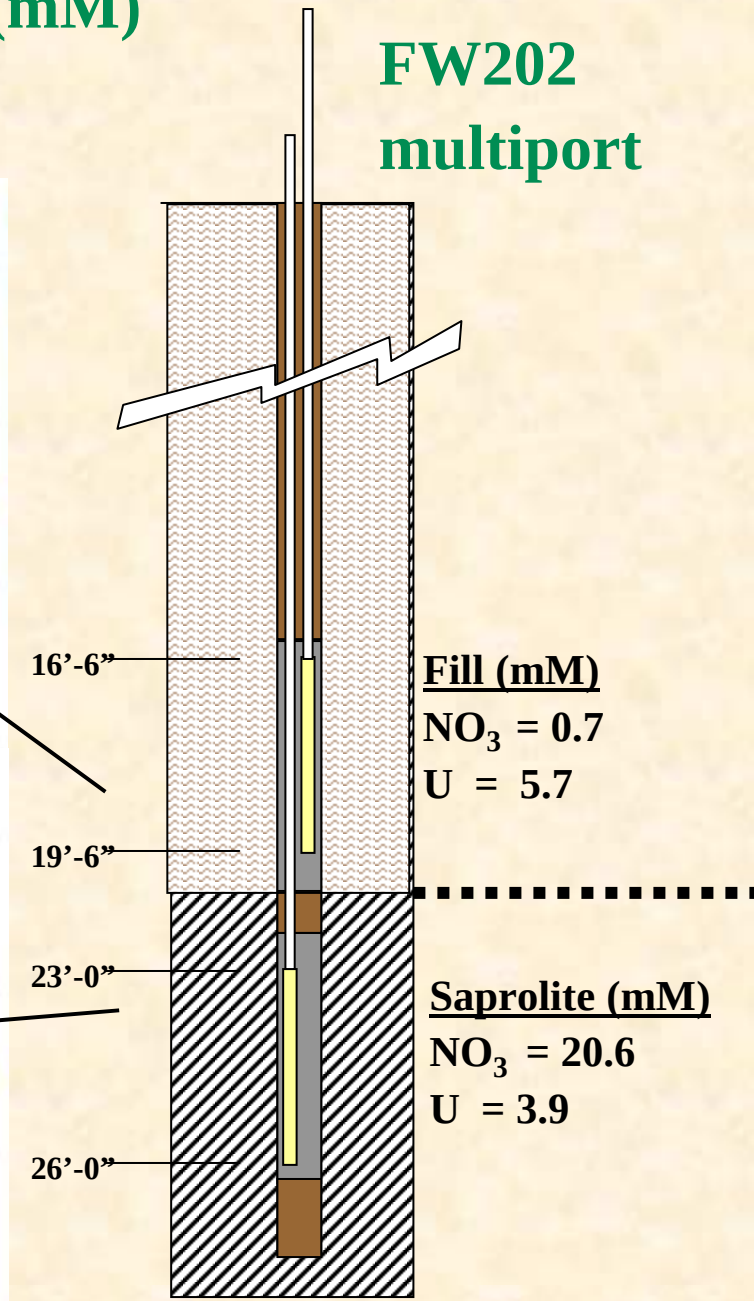




Groundwater Elevations at Area 2 September 9, 2003

AREA 2 - Distribution of Nitrate and U (mM)
- Nitrate is higher and U lower at depth



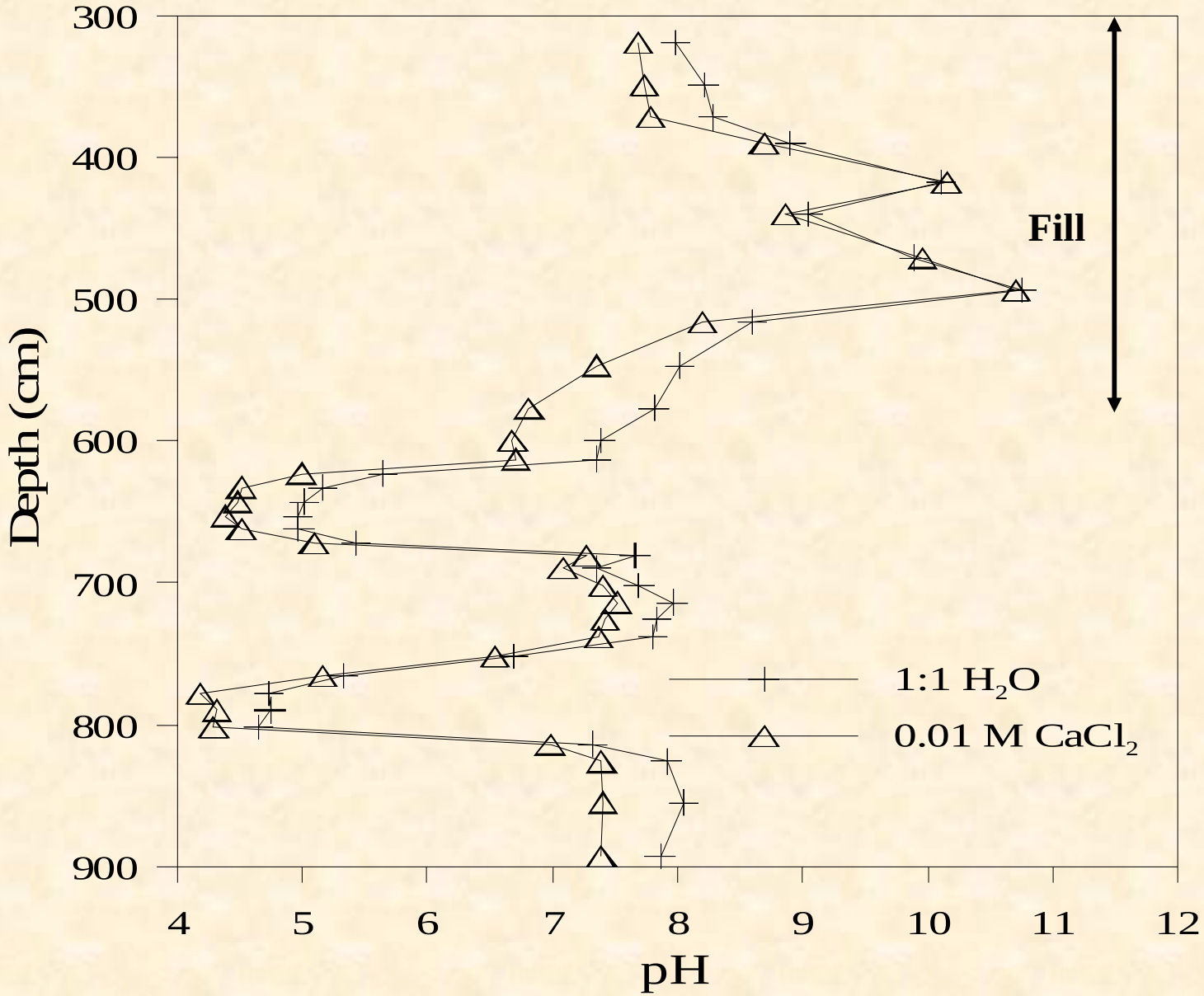


Characterization of FRC Cores Area 2

- **A corehole (FWB 200, Area 2)**
- **Analyses**
  - **Soil description**
  - **pH**
  - **Oxalate and CBD extractions (Fe, Mn, Al, U by ICP)**
  - **Uranium – Nitric acid extractable (ICP)**
  - **CEC – On-going (Cores from area 1, 2, and 3)**
- **Mineralogical Analyses**
  - **XRD and SEM-EDX analysis**
  - **Mineralogical characterization of manganese oxides – On-going**

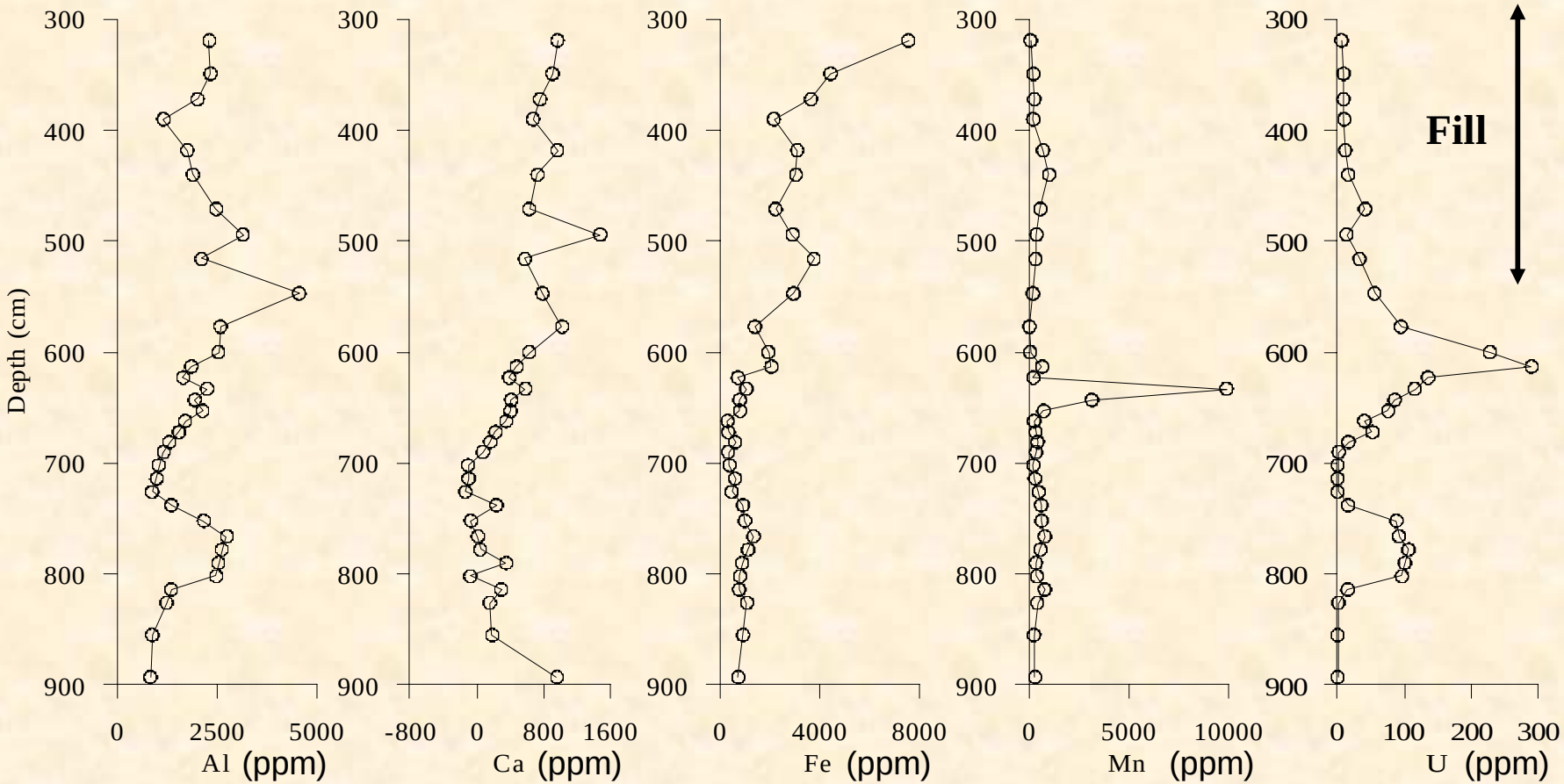
Soil pH

Core FWB200, Area 2, NABIR FRC Site



Oxalate Extractable Al, Ca, Fe, Mn, U

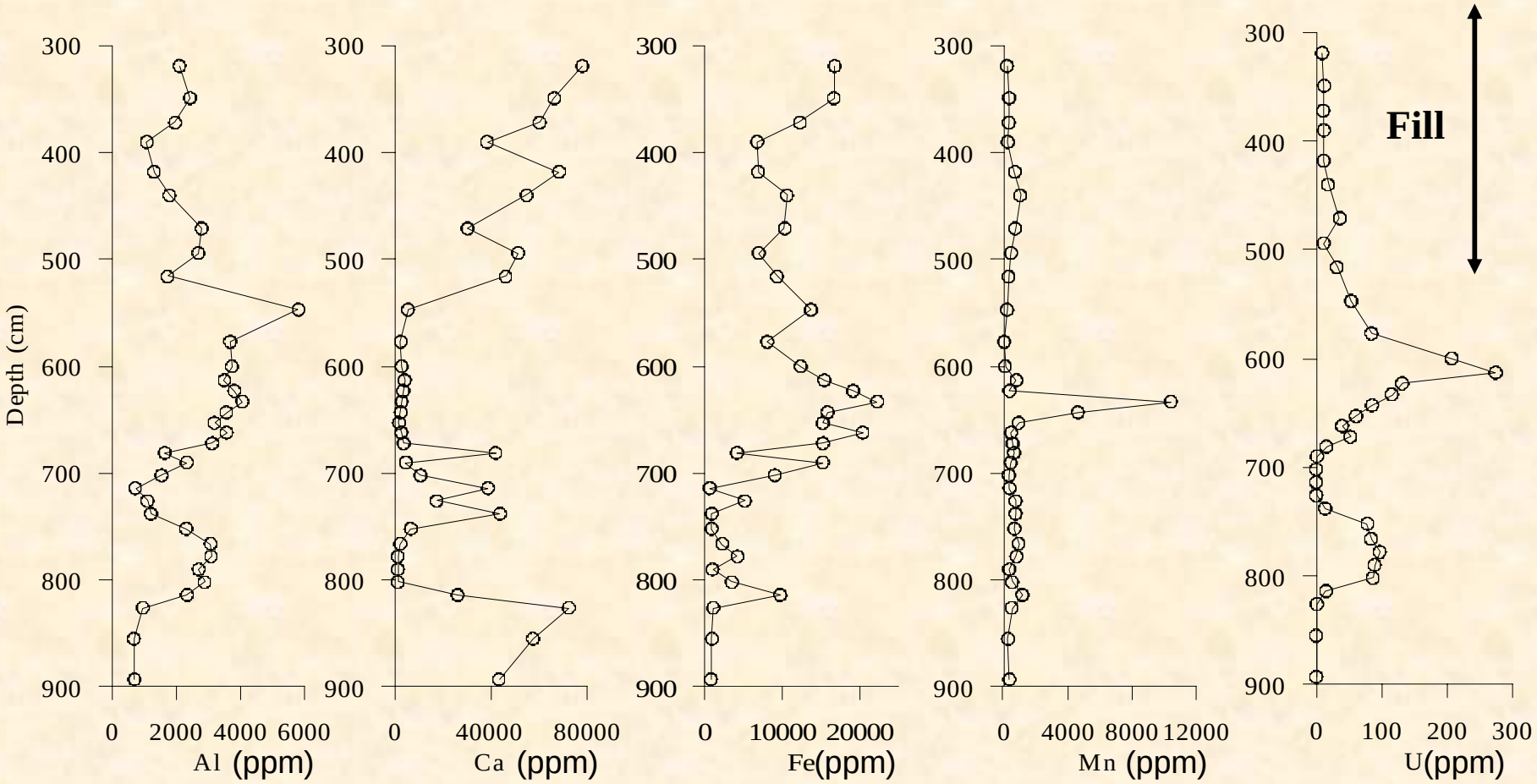
Core FWB200, Area 2, NABIR FRC Site (amorphous fraction)



CBD Extractable Al, Ca, Fe, Mn, U

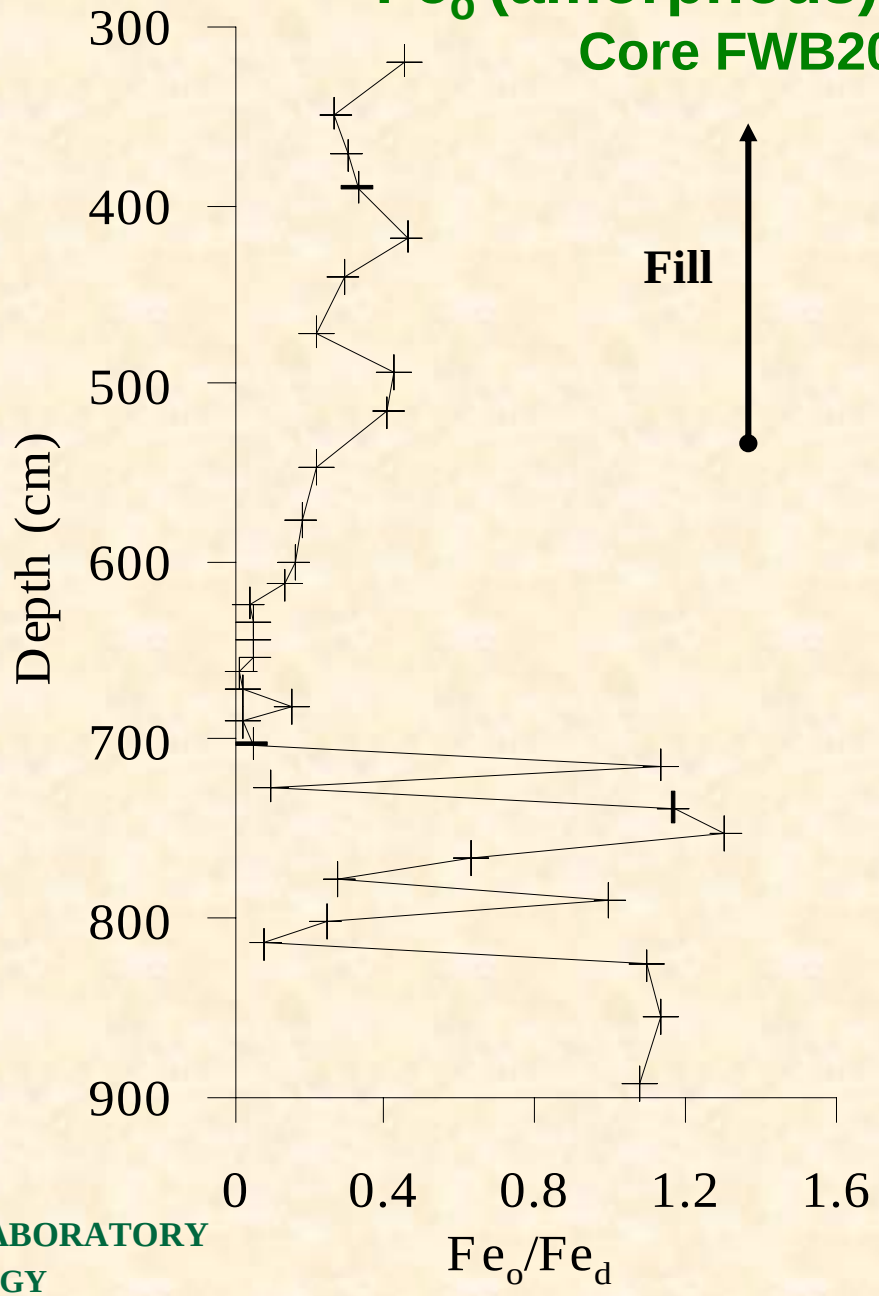
Core FWB200, Area 2, NABIR FRC Site

(crystaline fraction)



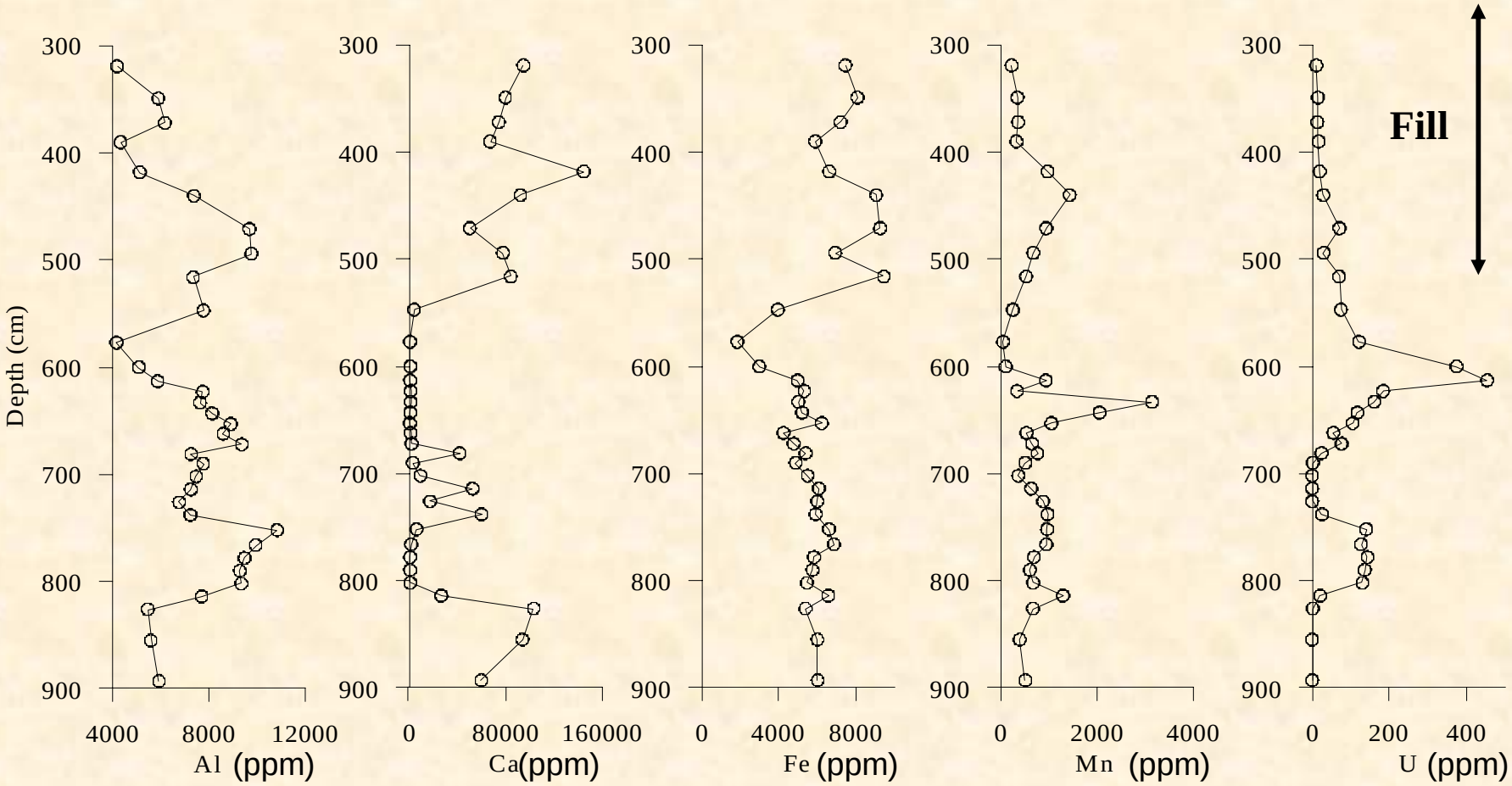
Fe_o (amorphous)/Fe_d (crytaline)

Core FWB200, Area 2



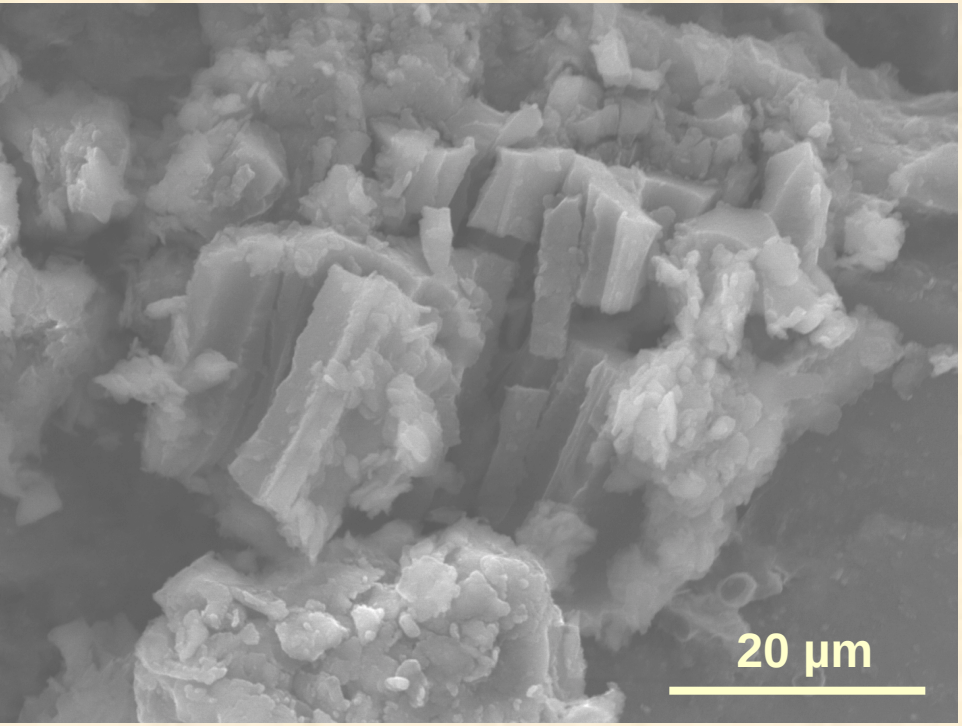
2N HNO_3- Extractable Al, Ca, Fe, Mn, U

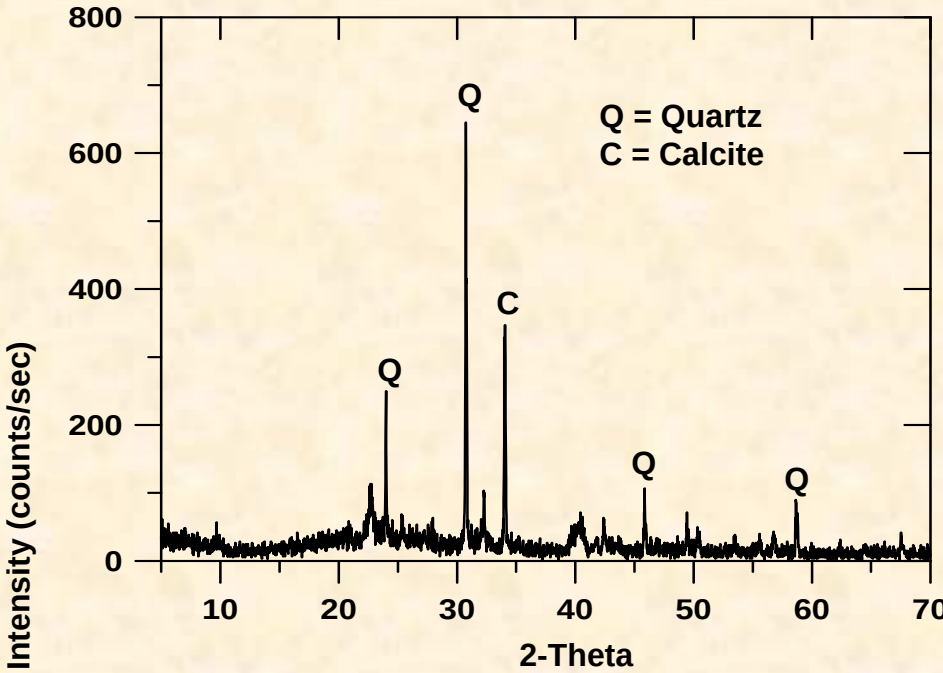
Core FWB200, Area 2, NABIR FRC Site



SEM and XRD Analysis of Calcite

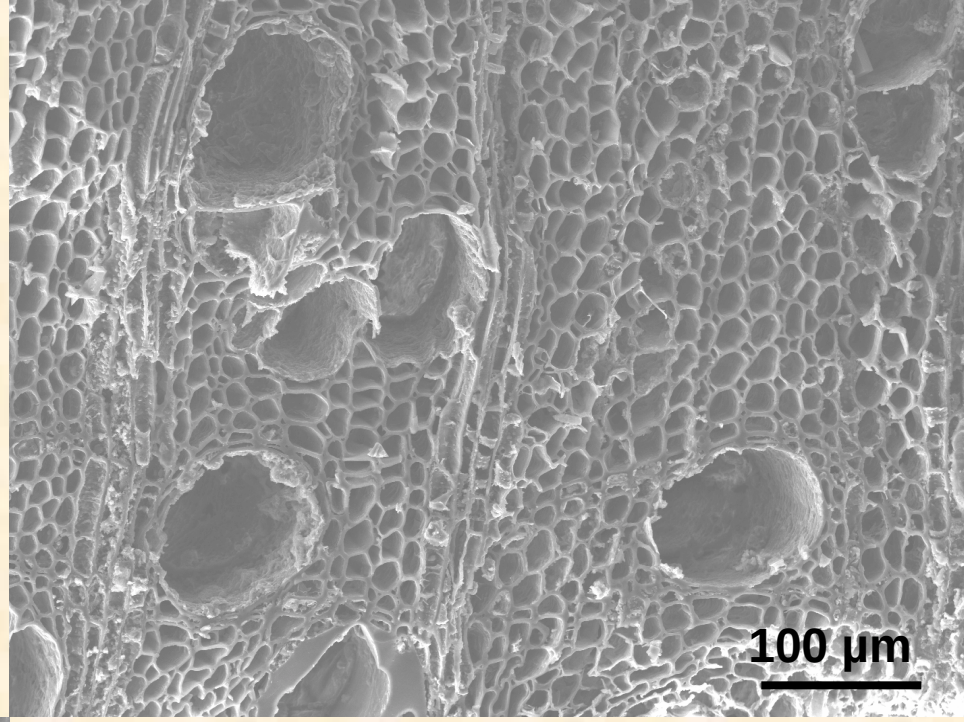
Core FWB200-05-00A (20 – 22.5'), Area 2, NABIR FRC Site

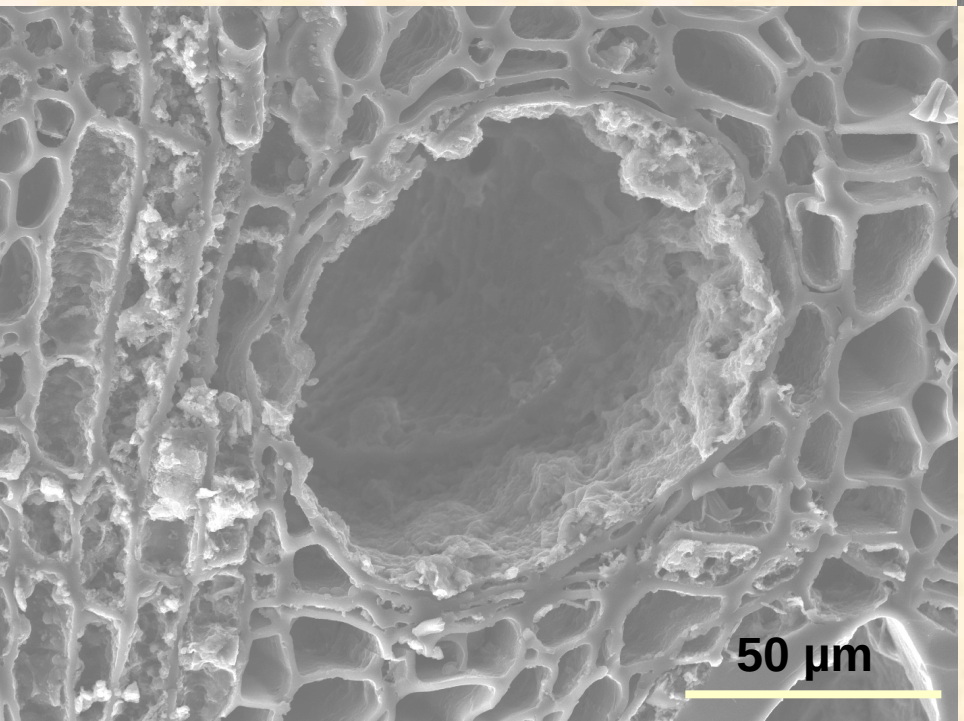


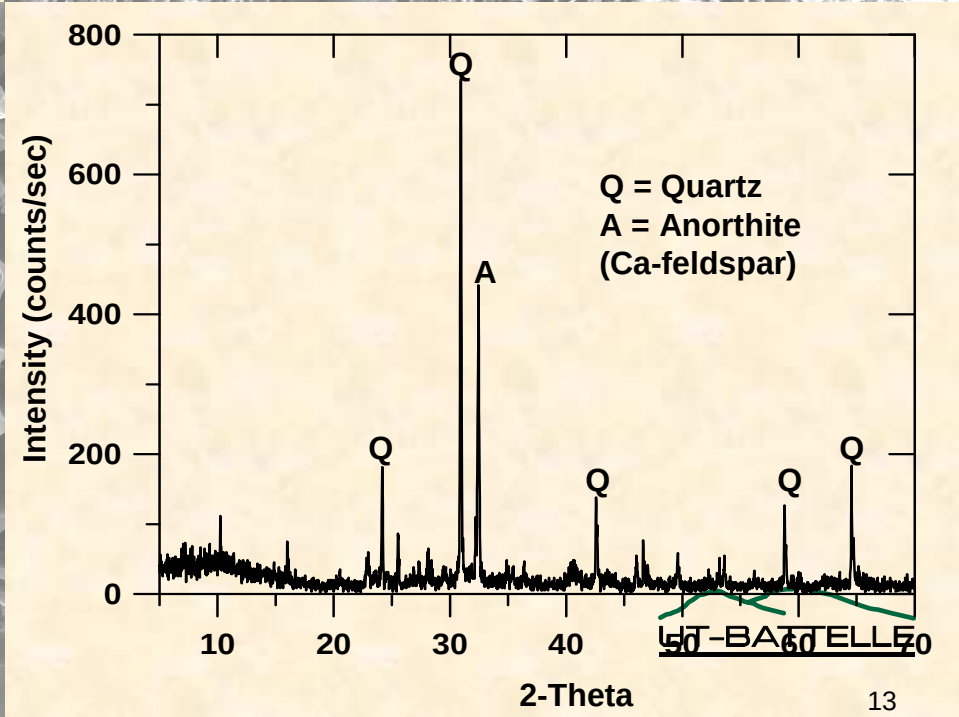


SEM and XRD Analysis of Ca-Feldspar (Anorthite)

Core FWB200-05-00A (20 – 22.5'), Area 2, NABIR FRC Site



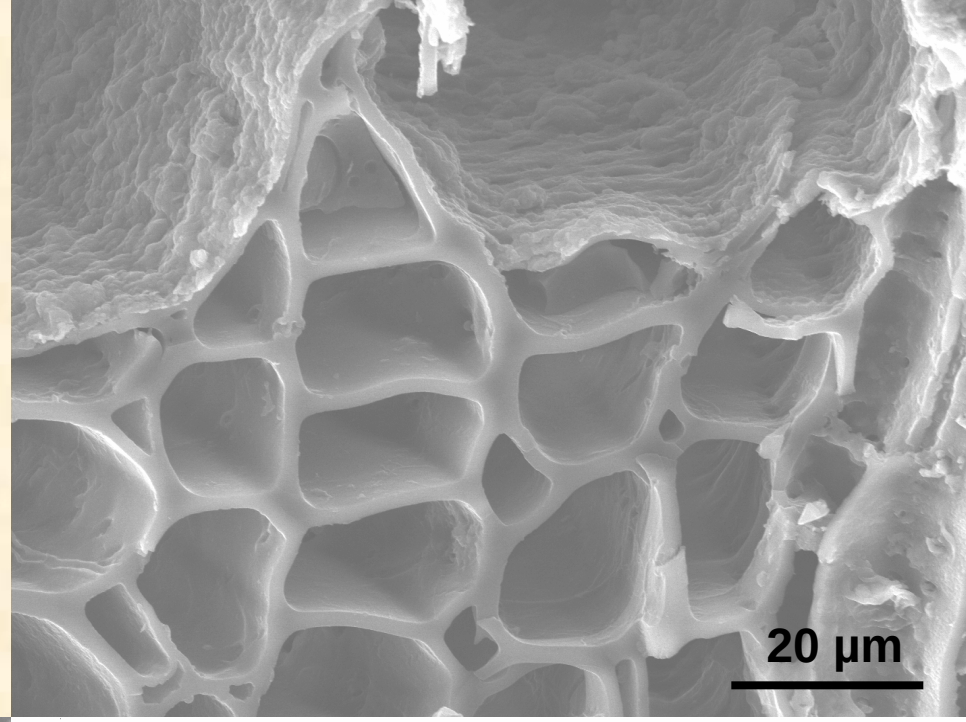


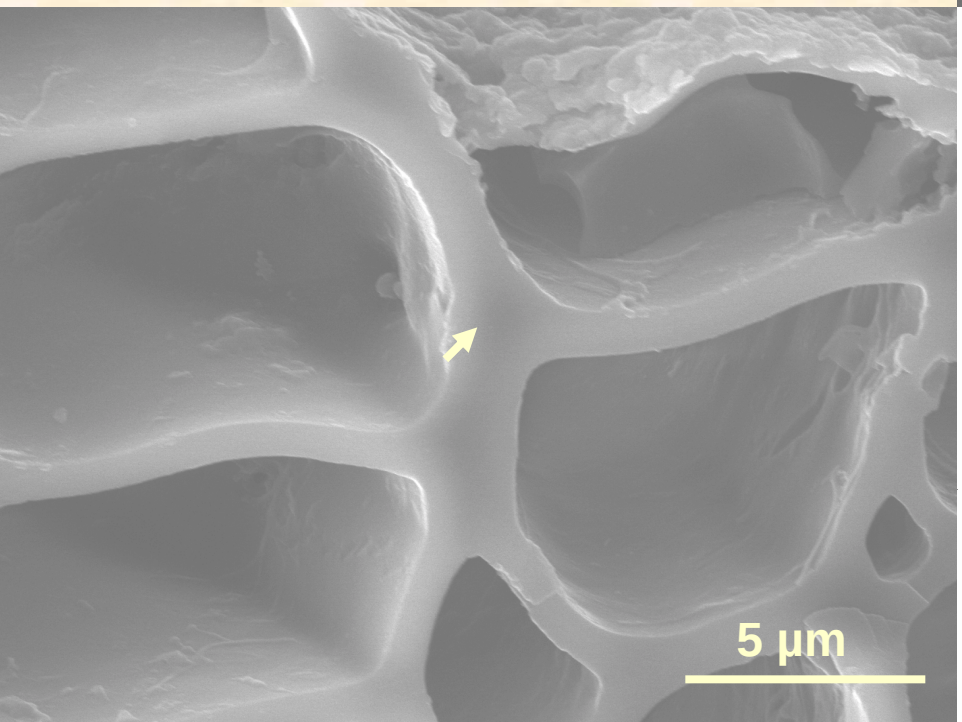


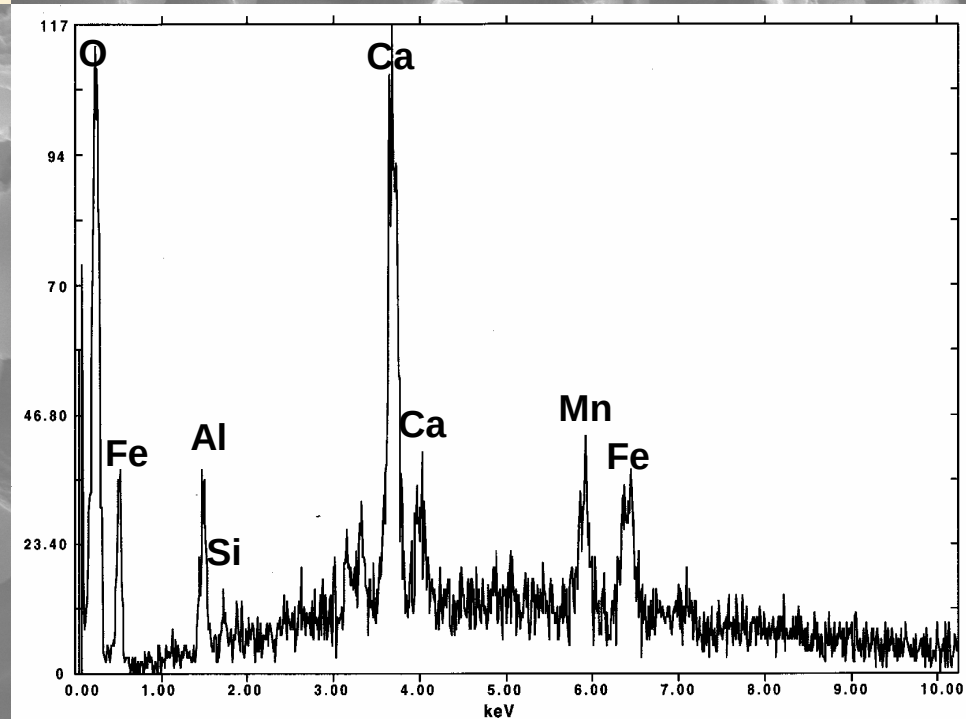
Field Research Center

SEM and EDX Analysis of Ca-Feldspar (Anorthite)

Core FWB200-05-00A (20 – 22.5'), Area 2, NABIR FRC Site

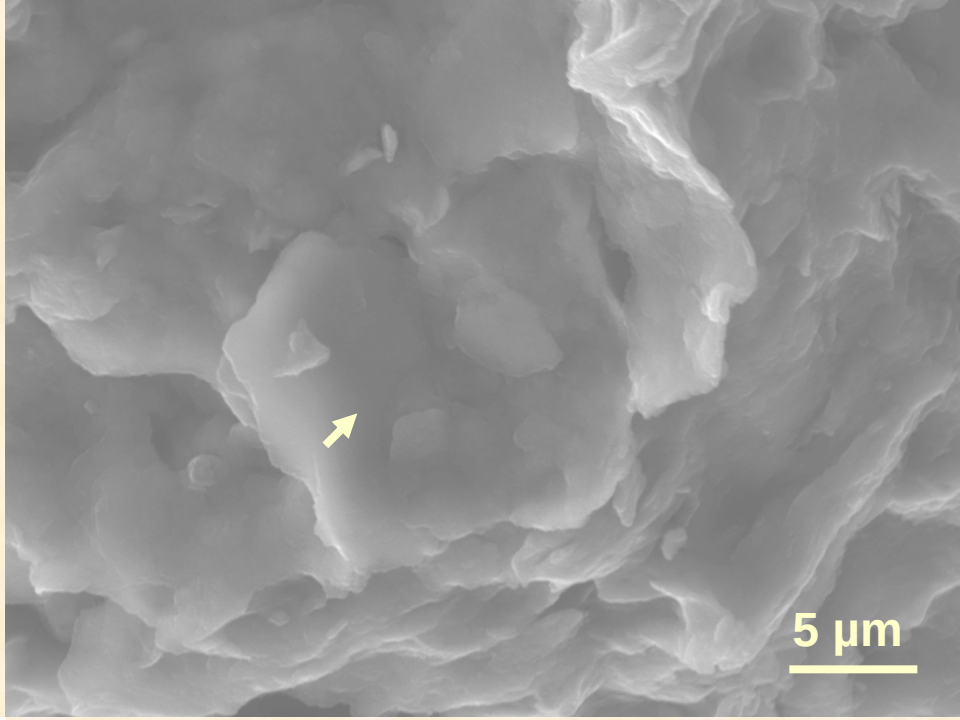


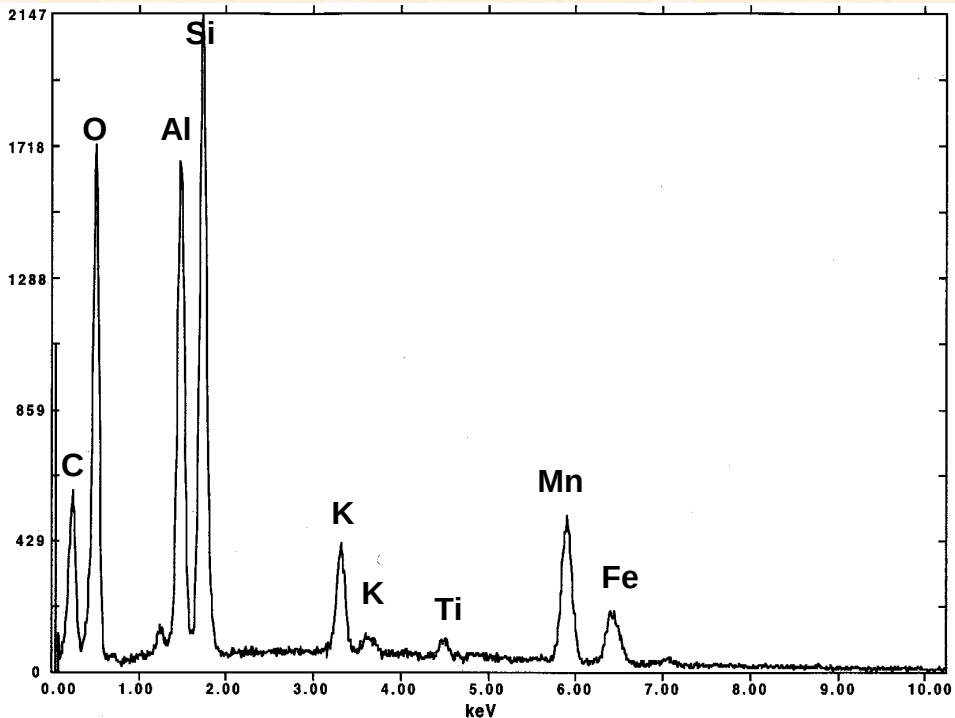


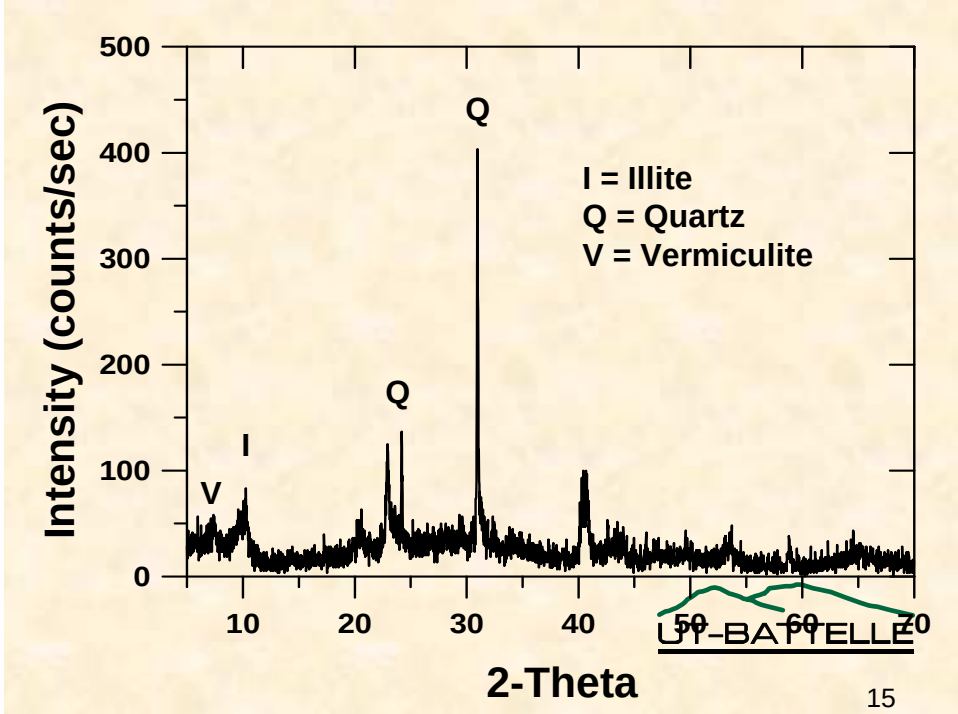


XRD, SEM and EDX Analysis of Illite (Aluminosilicate)

Core FWB200-05-00A (20 – 22.5'), Area 2, NABIR FRC Site



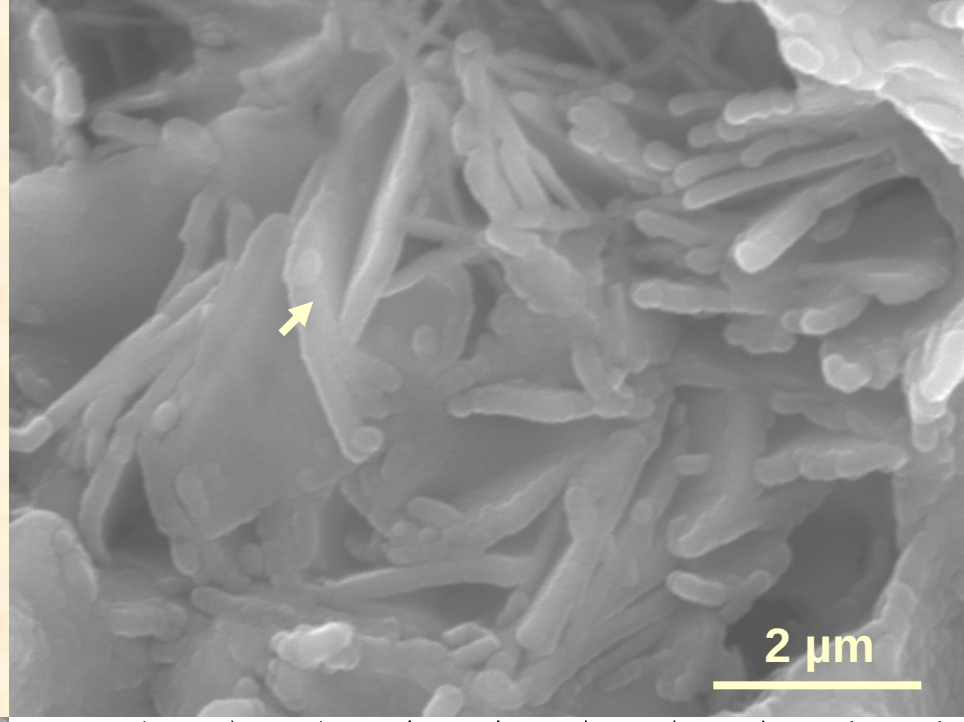


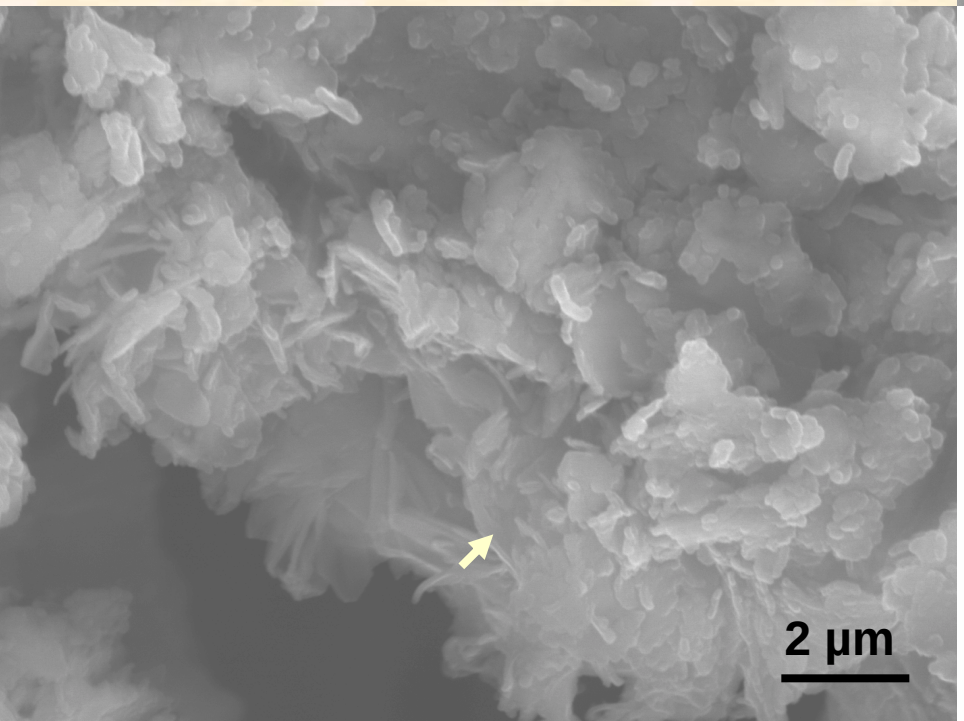


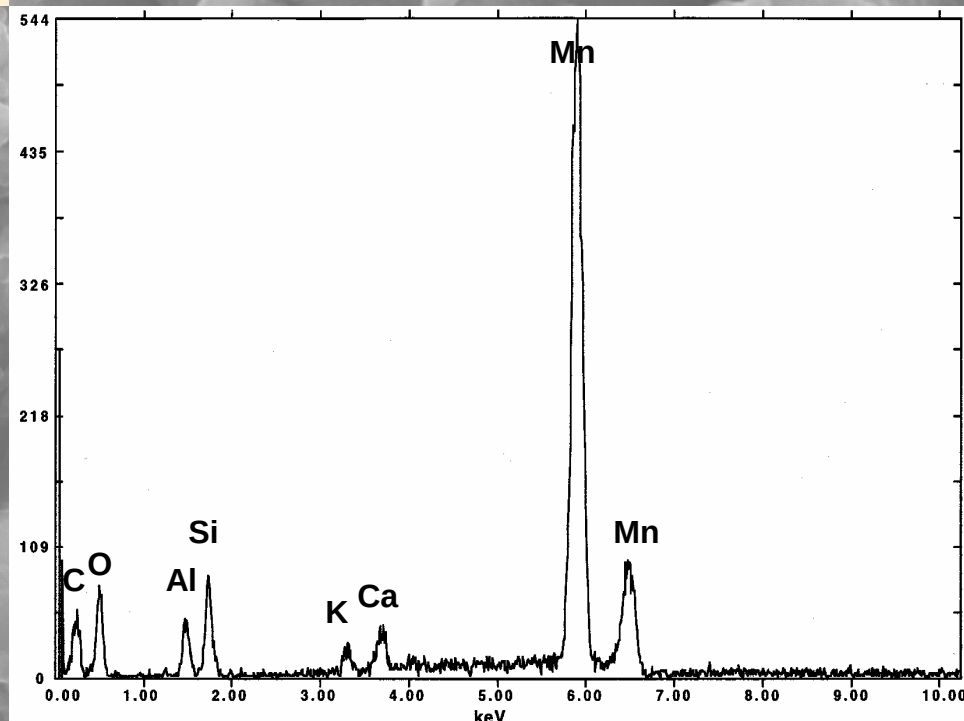
Field Research Center

SEM and EDX Analysis of Manganese Oxides

Core FWB200-05-00A (20 – 22.5'), Area 2, NABIR FRC Site

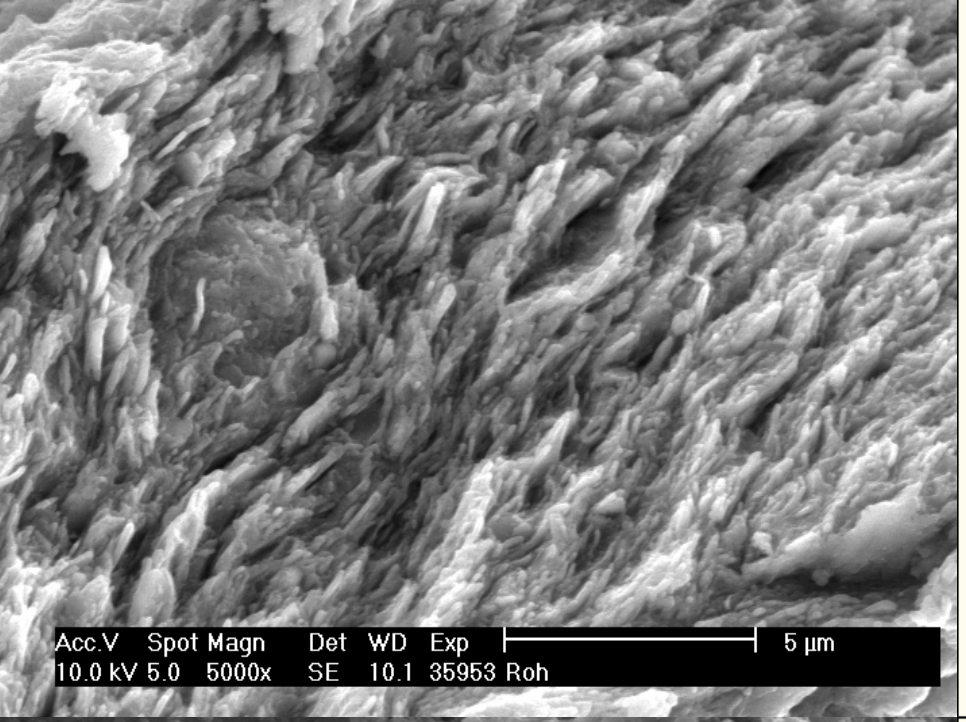


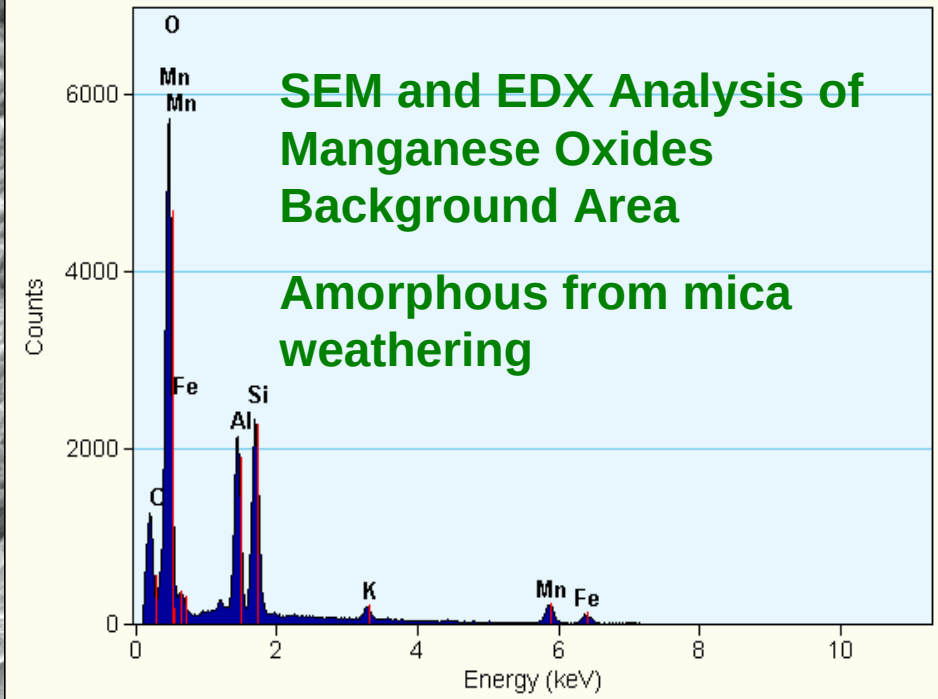


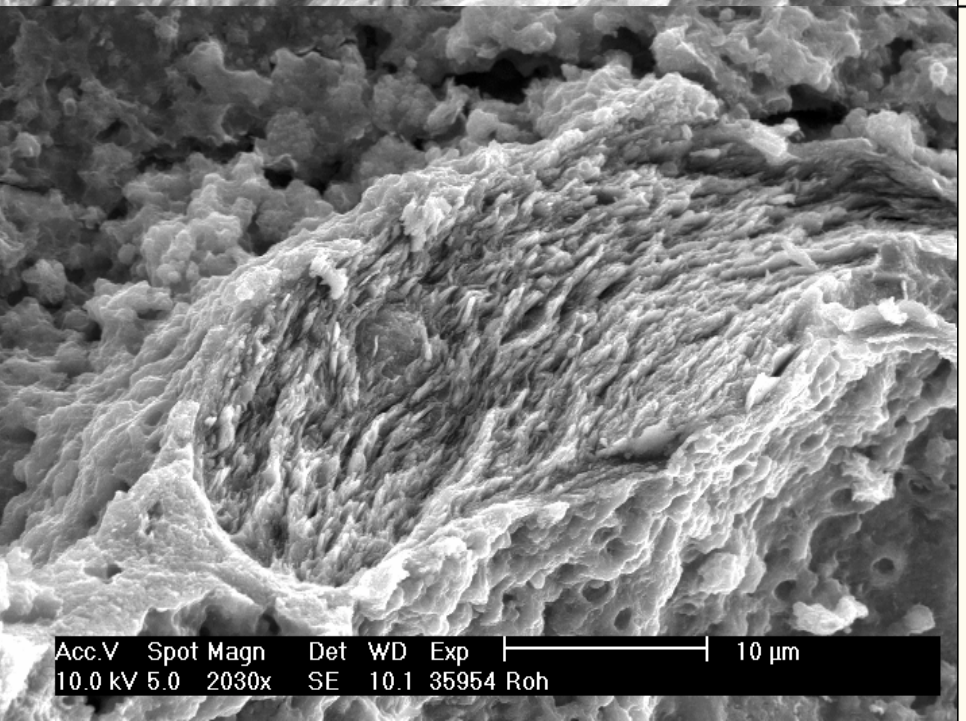


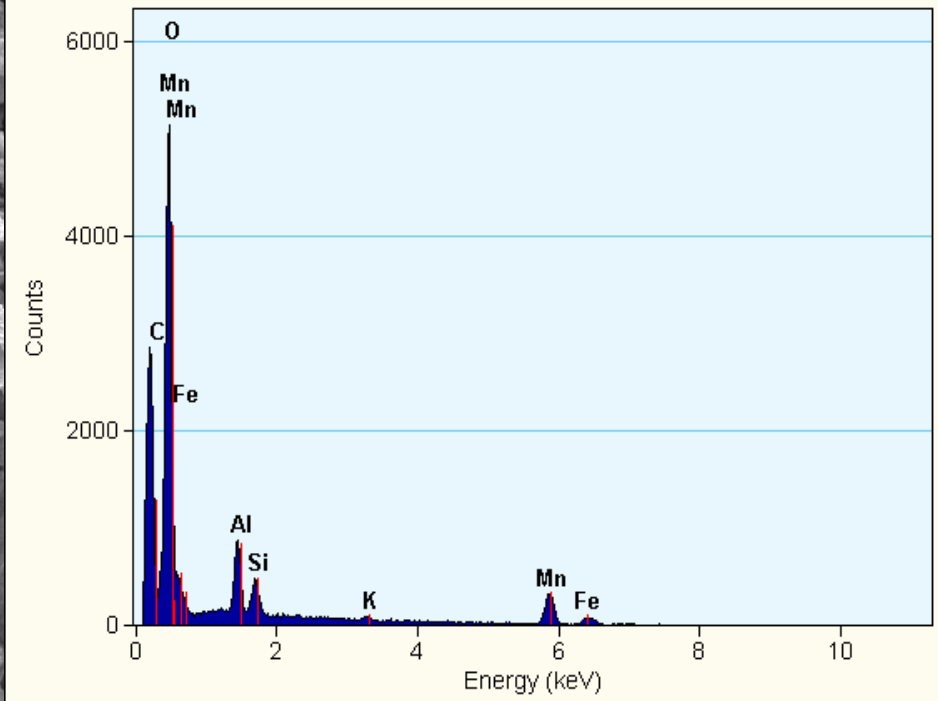
SEM and EDX Analysis of Manganese Oxides Background Area

Amorphous from mica weathering



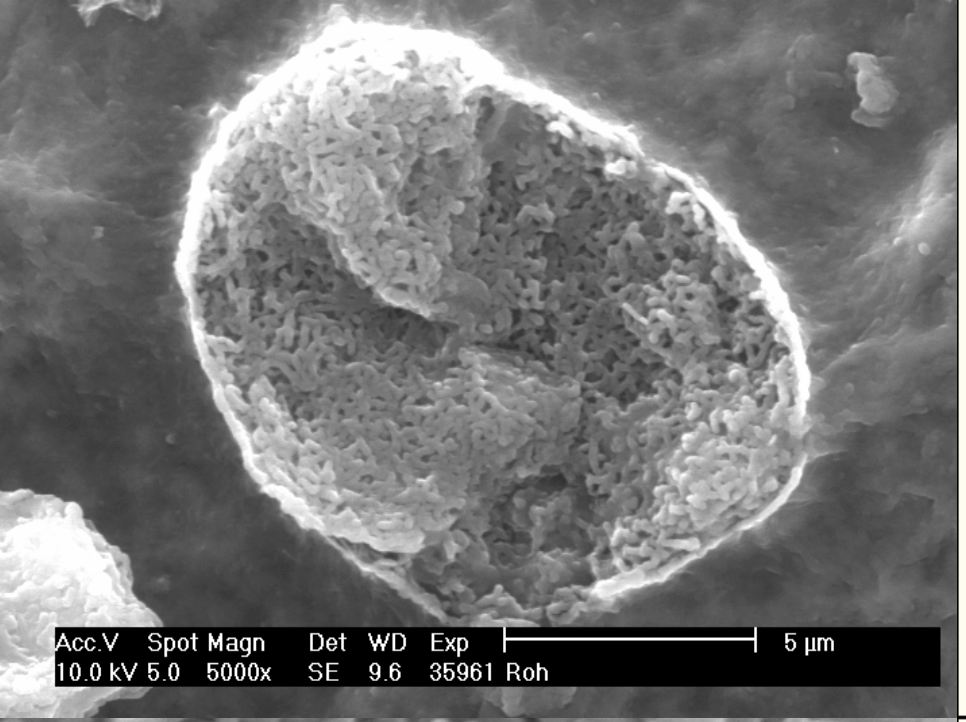


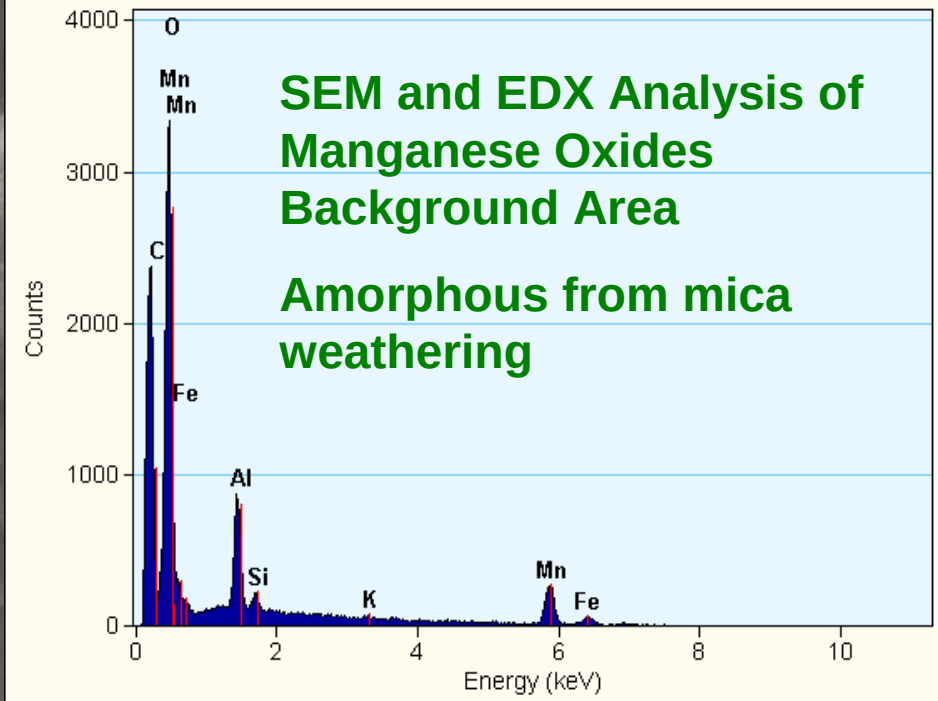


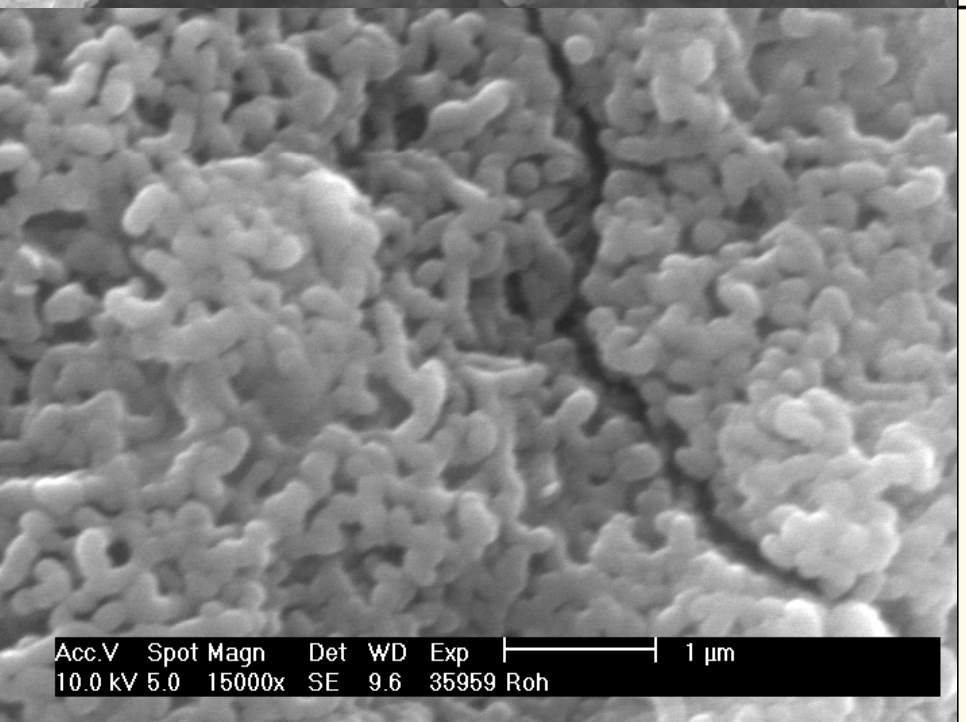


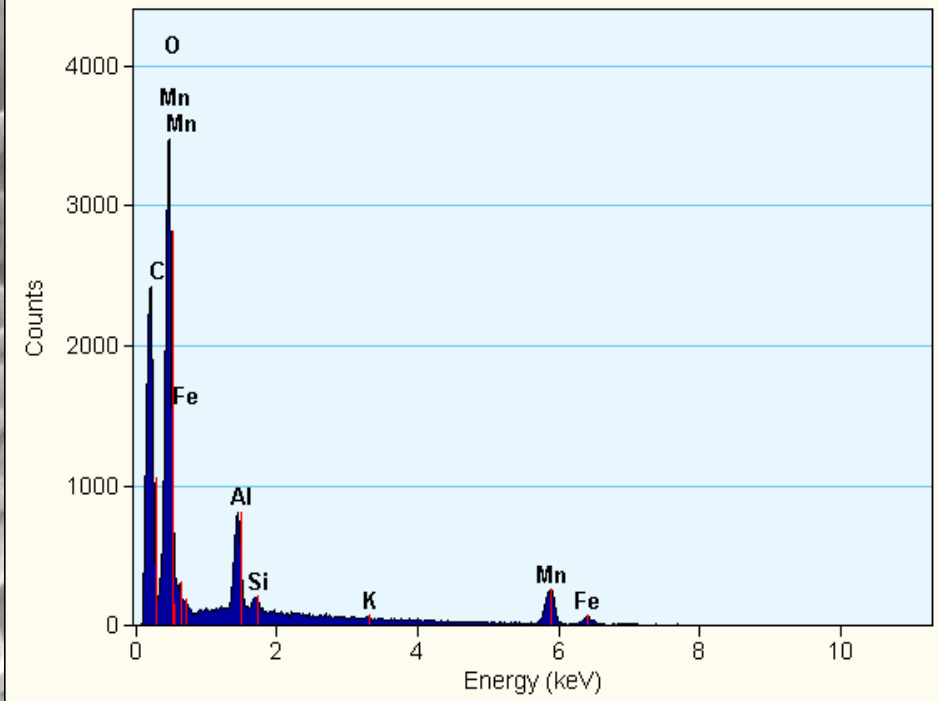
SEM and EDX Analysis of Manganese Oxides Background Area

Amorphous from mica weathering



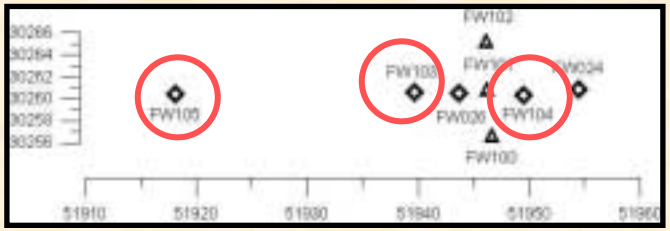






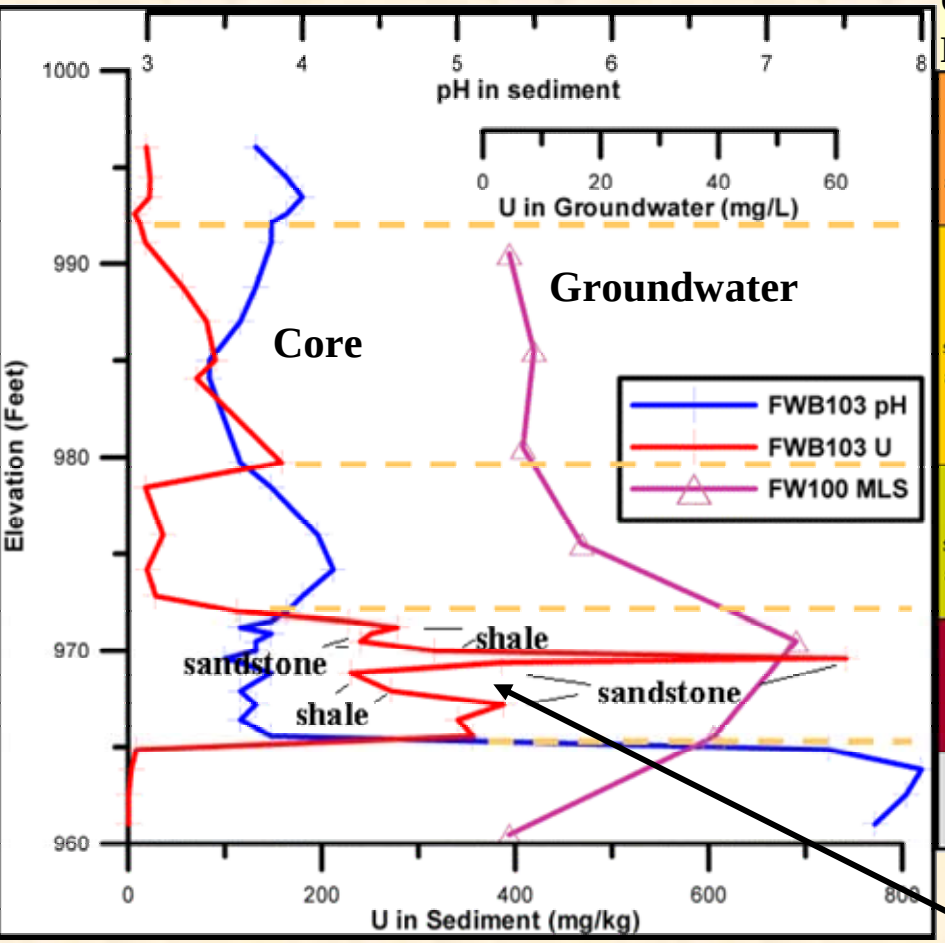
Characterization of Area 3 Cores (Phillips and Roh)

- **Three rotasonic coreholes to 15 meters (Area 3 Field Plot)**



- **Analyses**
  - **pH**
  - **Uranium (kpa)**
  - **Oxalate and CBD extractions (Fe, Mn, Al, Si by ICP)**
  - **P (fusion/ICP) and S (combustion infrared Leco)**
- **Mineralogical Analyses**
  - **Thin sections, SEM, EDX, BES element mapping**
- **EXAFS (ANL – Shelly Kelly and Ken Kemner)**

Rotasonic drilling in Area 3



Generalized Lithology

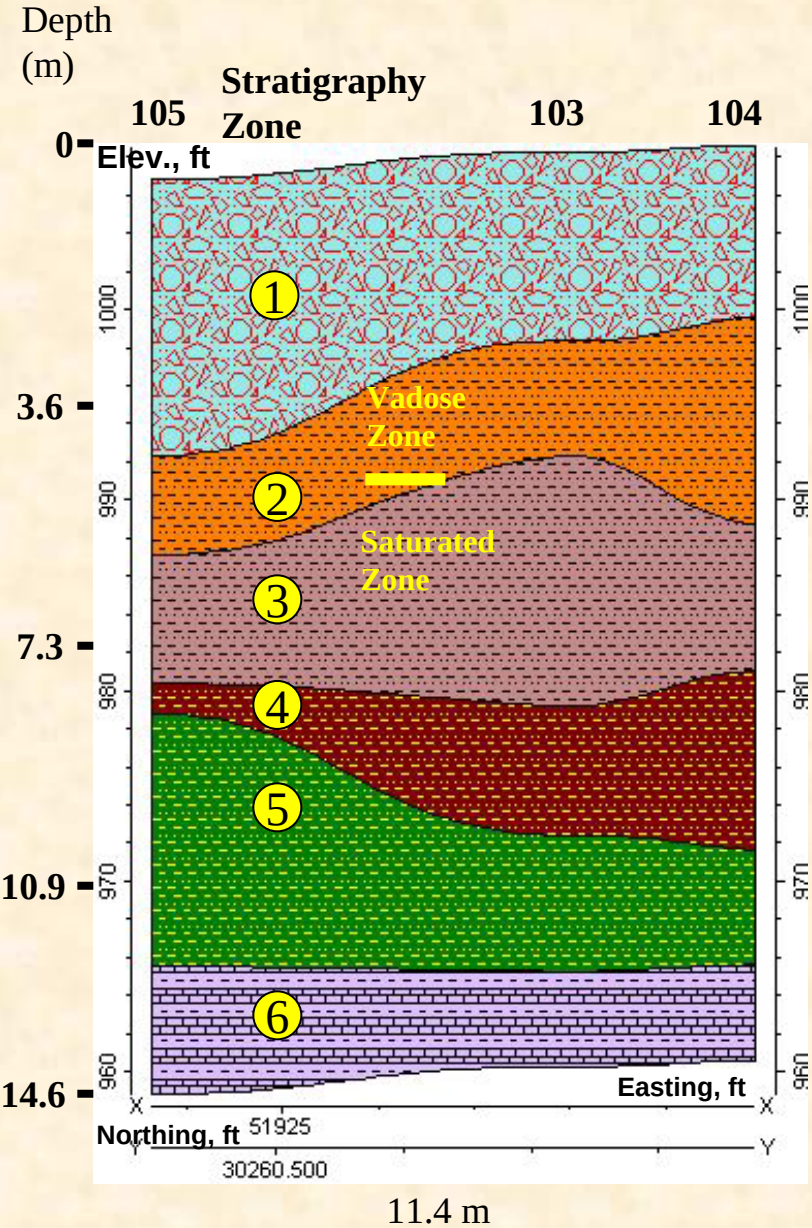
- Highly weathered shale and sandstone saprolite
- Moderately weathered shale, siltstone and sandstone saprolite
- Less weathered shale, siltstone and sandstone saprolite
- Weathered shale and sandstone
- Limestone and shale bedrock

Limestone zone

Mineral precipitation zone

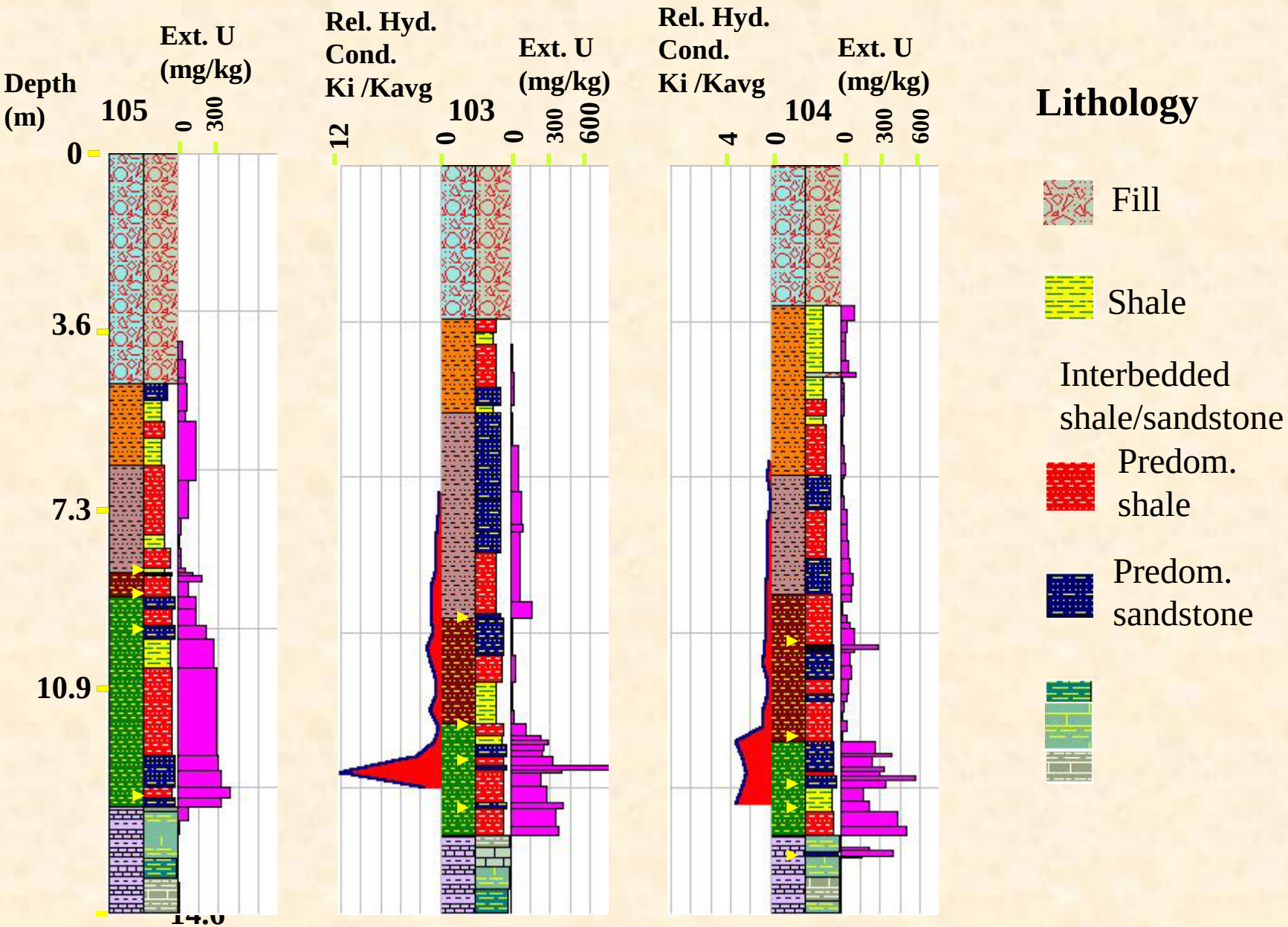
Uranium and pH on Sediment compared to U in Groundwater Area 3 Field Plot (FWB103)

General Description and Interpolation of the Stratigraphy between the Cores



General Stratigraphy	Zone	Description		
Fill	1	Mixture of limestone, soil and saprolite		
		Rock	Major Color	Moist Consistence
Interbedded Shale and Sandstone Saprolite	2	Shale	7.5YR 5/6	V. friable-friable
		Sandstone	10YR 5/4	V. friable-firm
	3	Shale	7.5YR 5/6, 2.5Y 5/4	V. friable-friable
		Sandstone	10YR 4/4	V. friable-firm
	4	Shale	2.5Y 5/4	Friable
		Sandstone	10YR 4/3	Friable-firm
	5	Calcareous Shale	2.5Y 5/4, 5/2	Friable-firm
		Sandstone	5YR 2/1	Ex. Firm
Interbedded Limestone, Shale and Sandstone Bedrock	6	Limestone	--	Ex. Firm
		Shale	--	Ex. Firm
		Sandstone	--	Ex. Firm

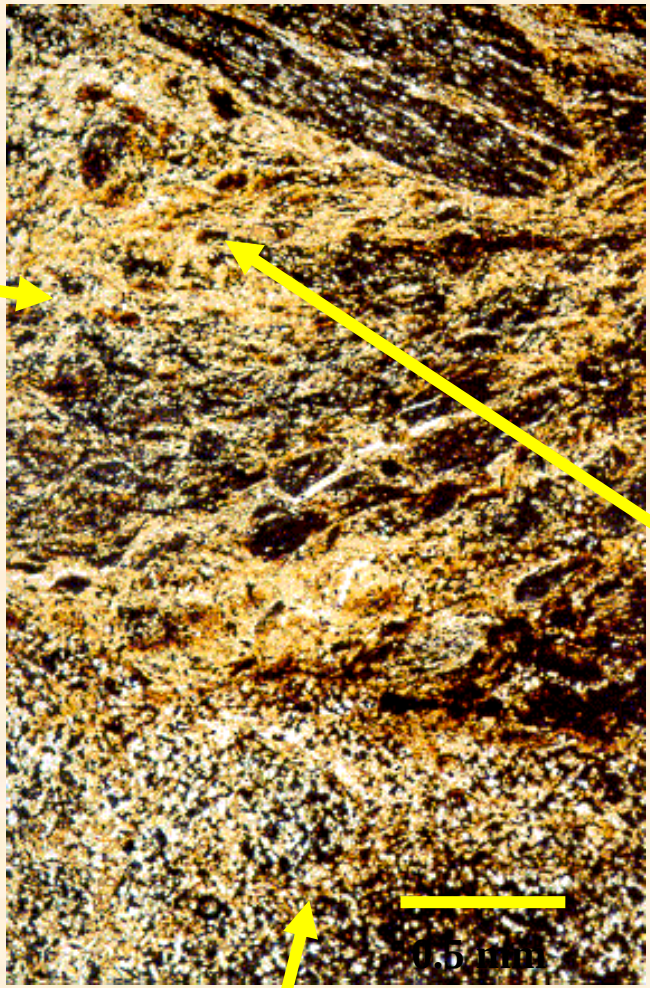
Distribution of Extractable U and Relative Hydraulic Conductivity in the Cores



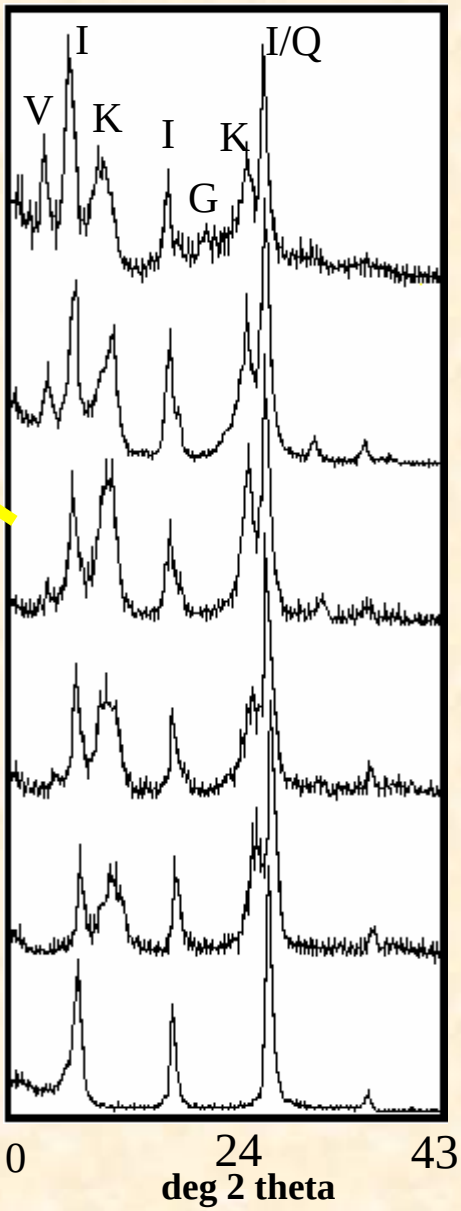
Increases of U at discontinuities

Differential Weathering of Interbedded Shale and Sandstone

Highly weathered shale



Clay Mineralogy (XRD)



Illite≥Kaolinite>Vermiculite>Geothite>Quartz

Untreated-25ºC

Mg sat

Mg sat-gly

K sat-25ºC

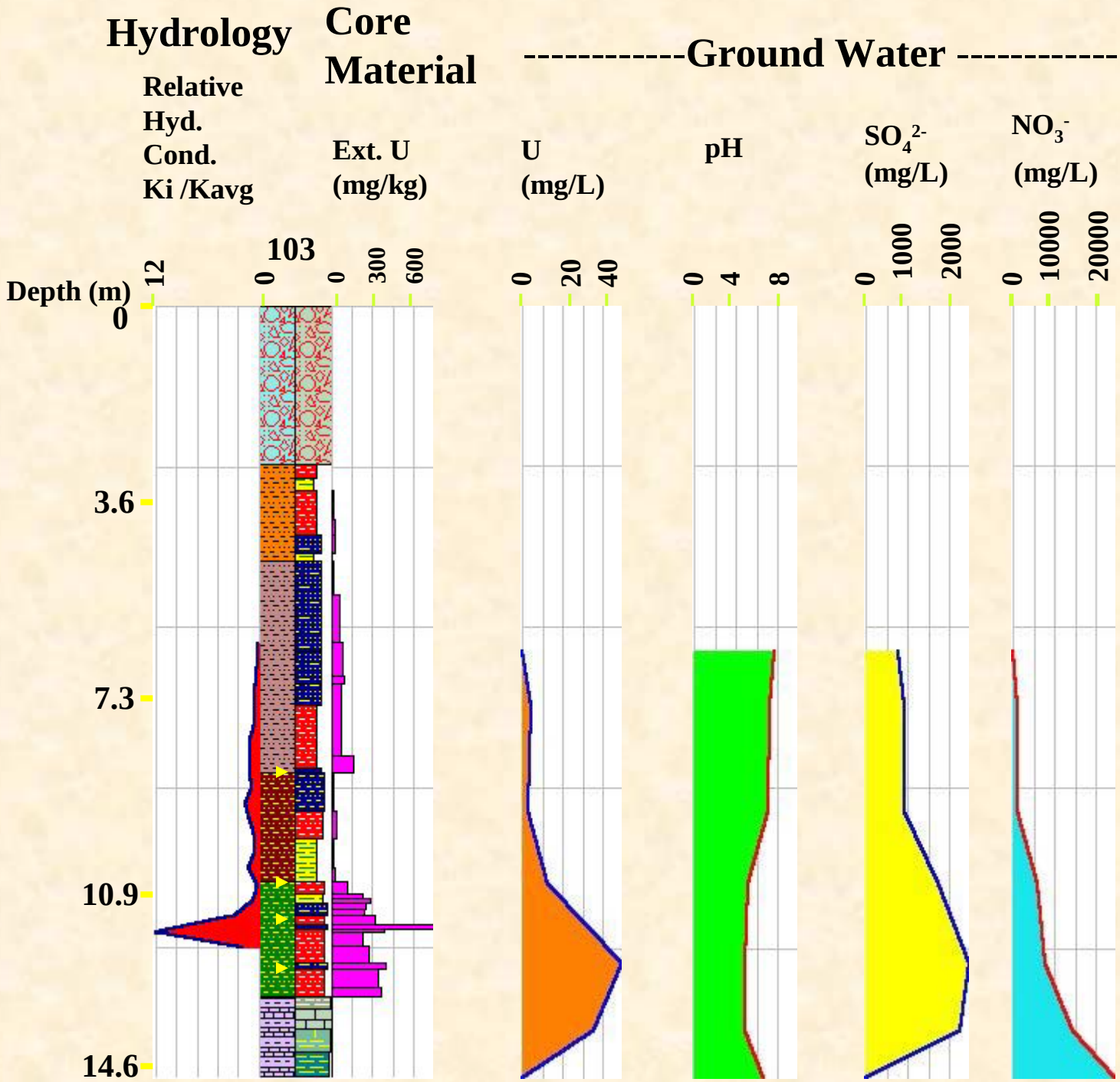
K sat-300ºC

K sat-550ºC

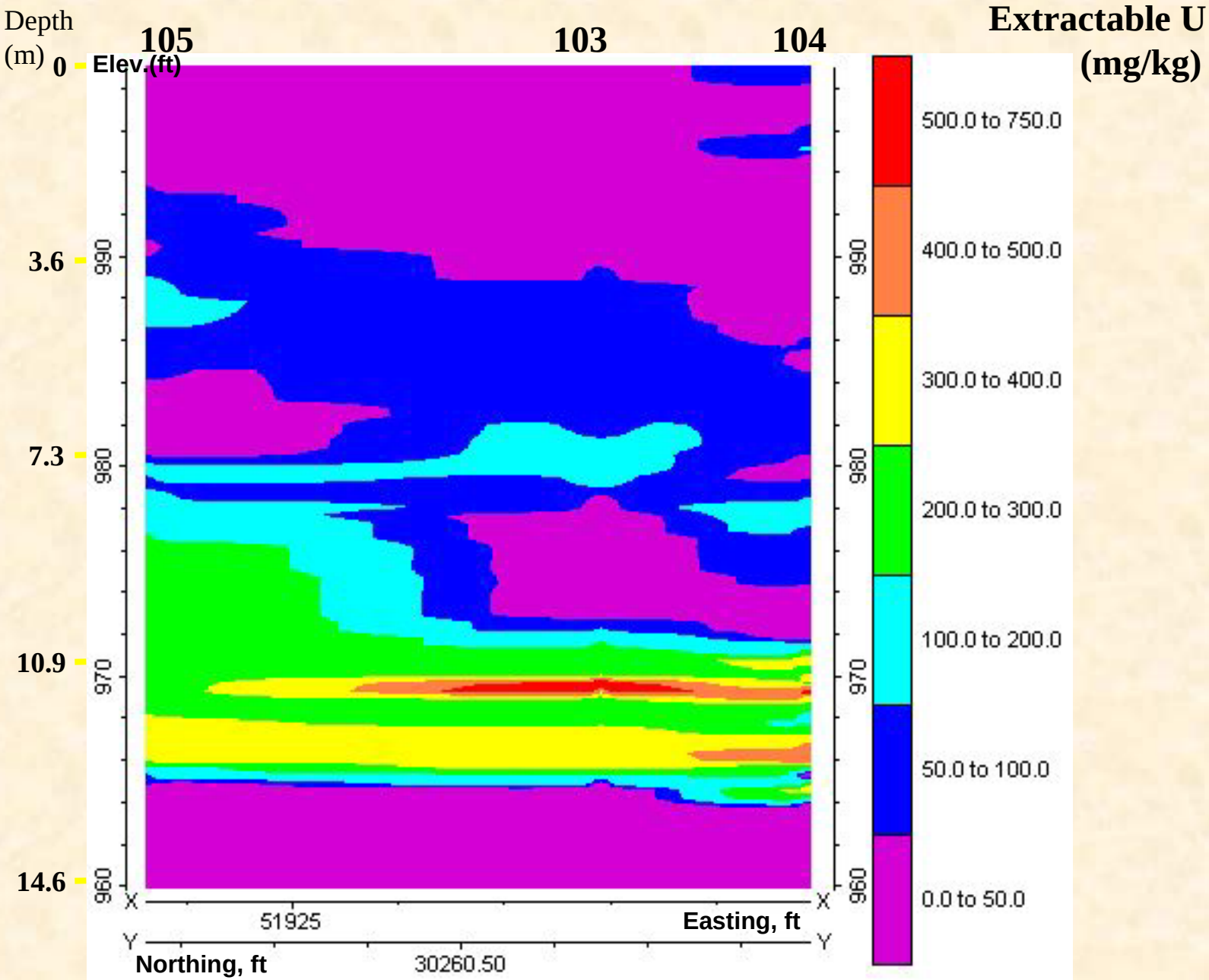
pH 3.4-4.2 above the limestone

Fed 0.7-2.9%
Mnd 0.004-0.68%
Ald 0.06-0.45%

Sandstone

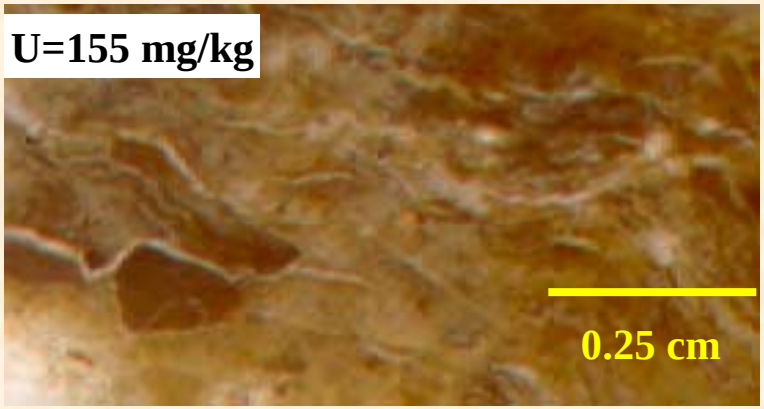

Hydrology
Core Material
----------Ground Water ----------
Relative Hyd. Cond. Ki /Kavg
Ext. U (mg/kg)
U (mg/L)
pH
SO_4^{2-} (mg/L)
NO_3^- (mg/L)
103
Depth (m)
12
0
0
300
600
0
20
40
0
4
8
0
1000
2000
0
10000
20000
0
3.6
7.3
10.9
14.6

Interpolated Uranium Distribution between the Cores

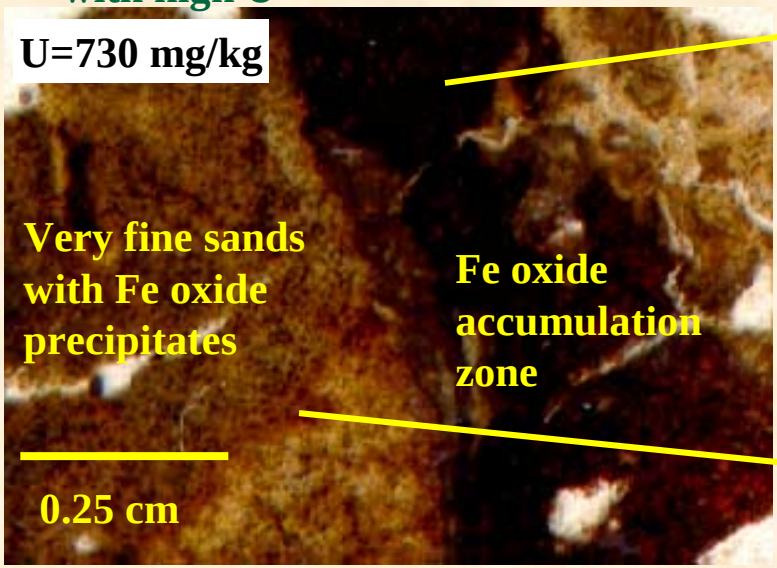


Area 3 Core Mineralogical Evaluations

Overlying highly weathered gleyed leached shale



Black precipitate zone in sandstone with high U

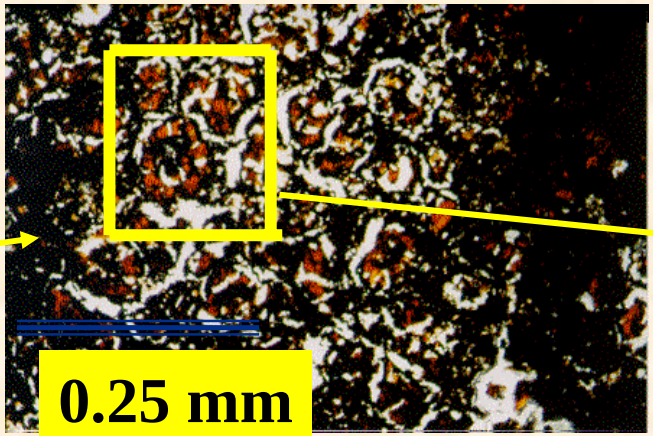


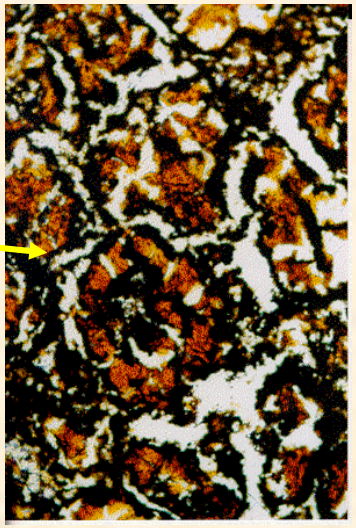
A high U zone was detected in FW100 (Area 3 field site) at a depth of 46'.

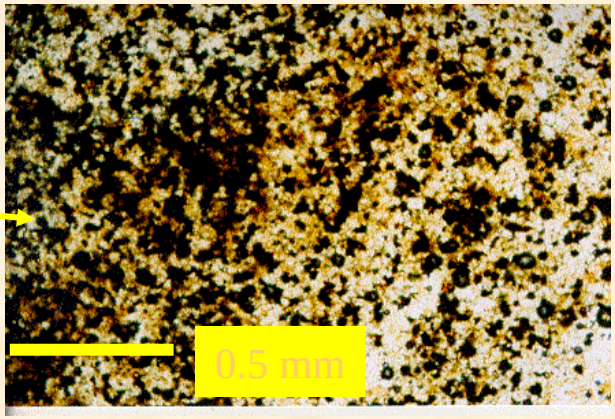
XRD results:

Gleyed Zone - Quartz, Vermiculite, Mica, HIV, Ca-feldspar

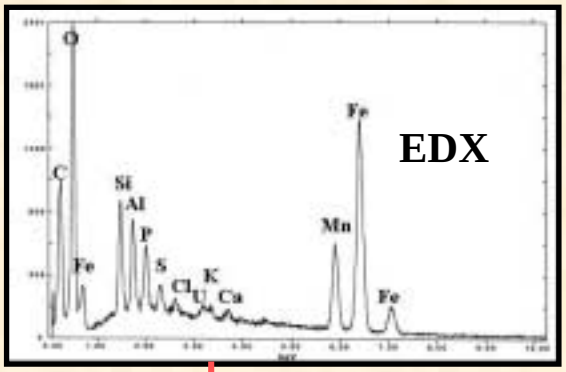
Black Zone - Quartz, Ca-feldspar, Vermiculite, Mica, Goethite



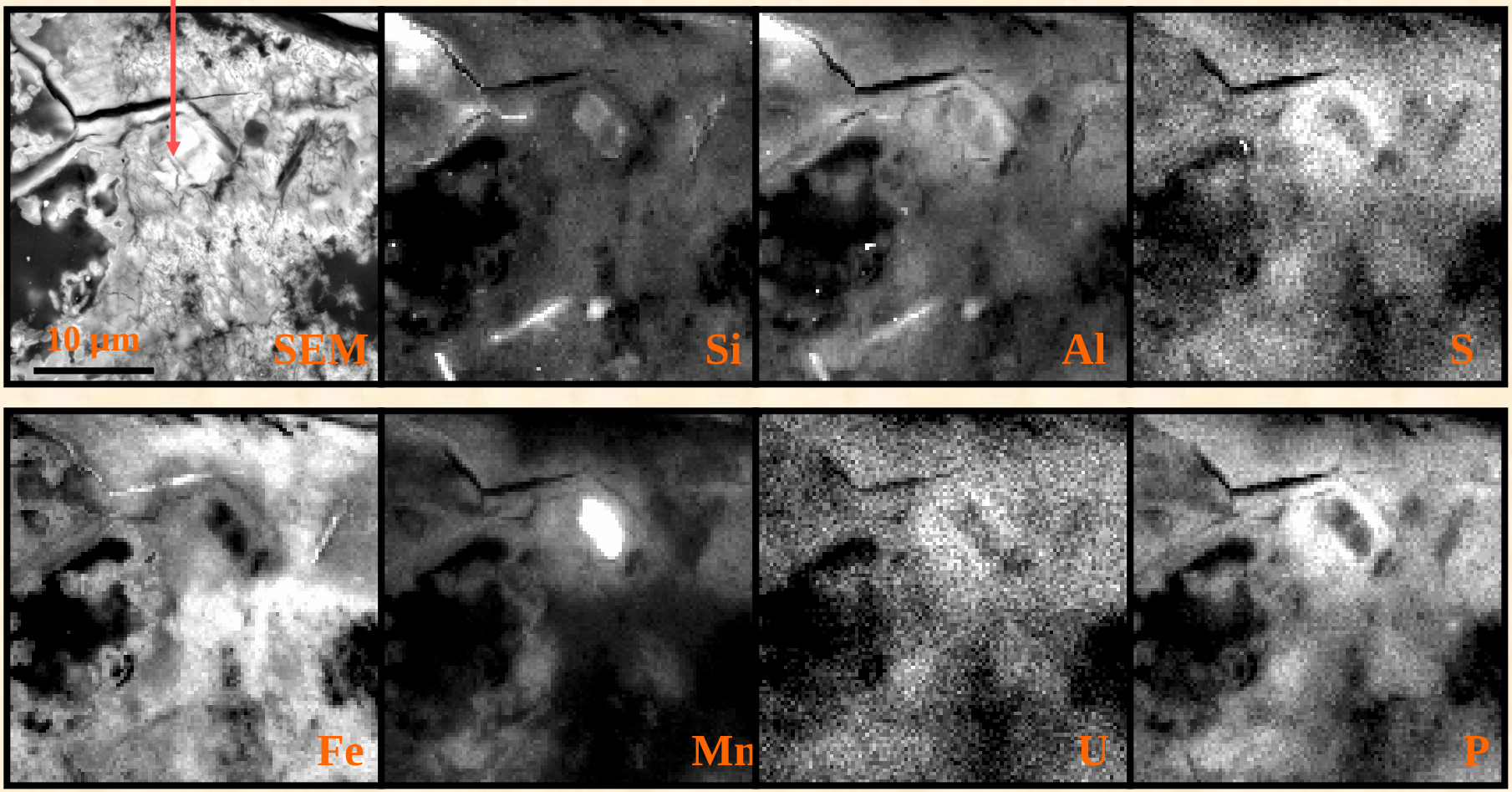




SEM-BSE-Element Mapping of FWB100-06-09 sample Black high U zone



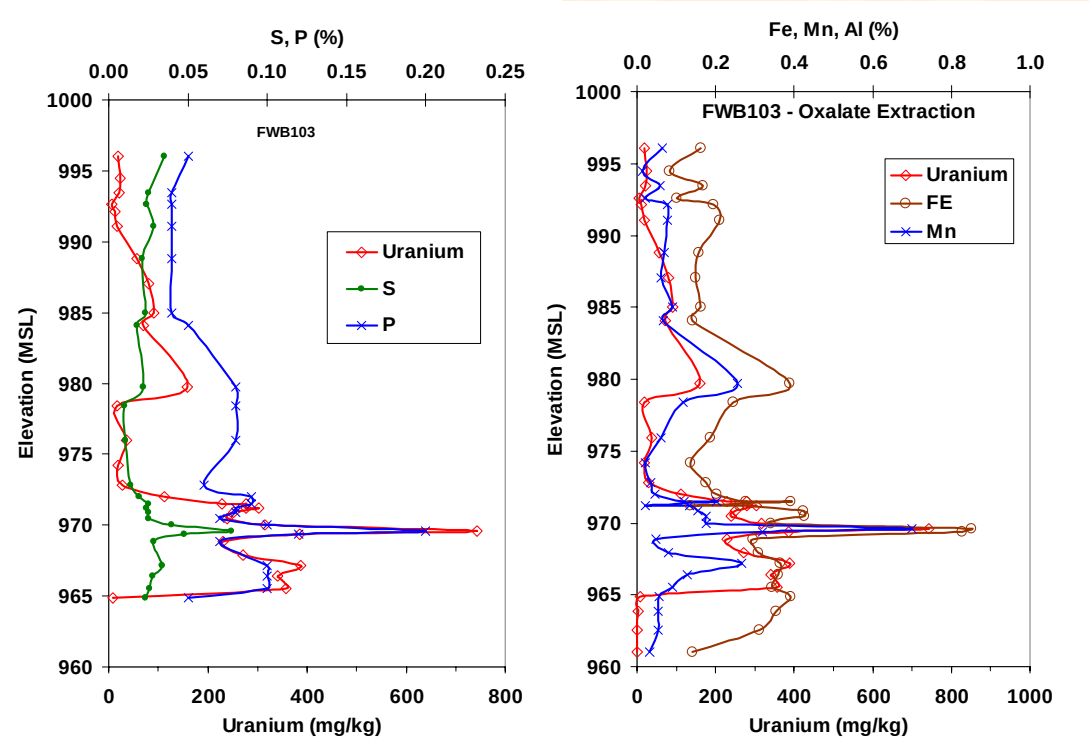
U distribution matches P and S distribution



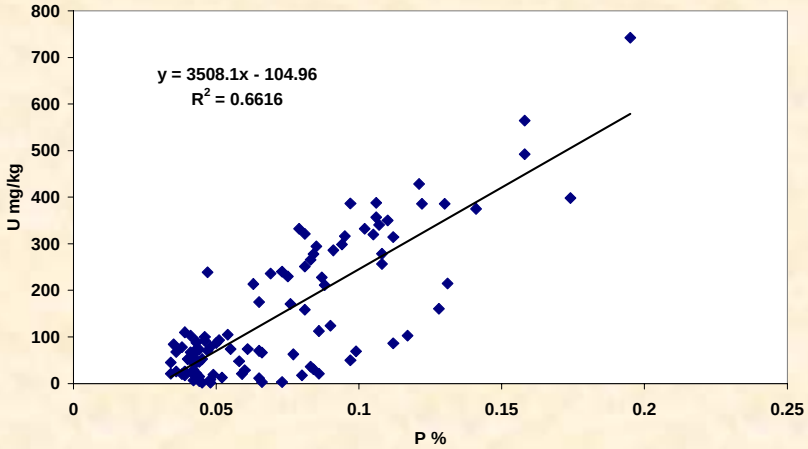
Core Analysis (Fe, Mn, Al, P, S)

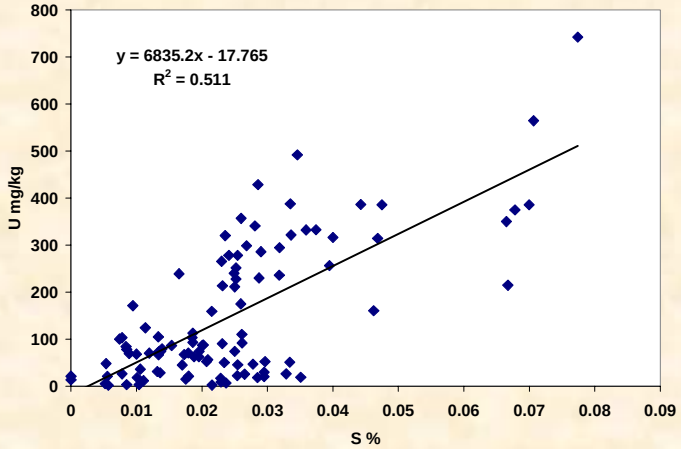
- Correlation varies form core to core and between depth intervals
- P is as high as 0.2 %
- P and S are correlated to U

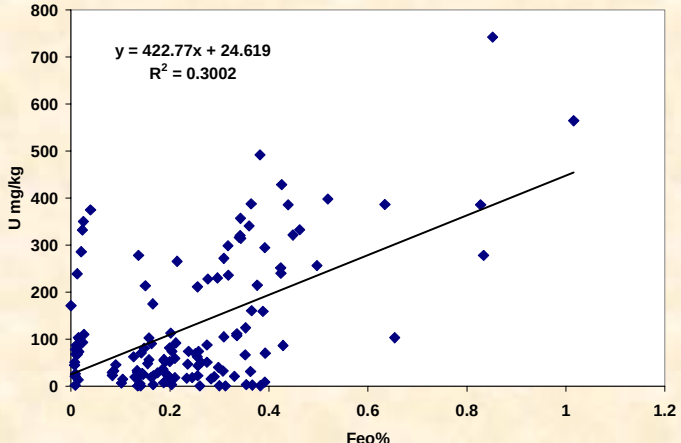
FW103 distribution with depth - Strong association with U

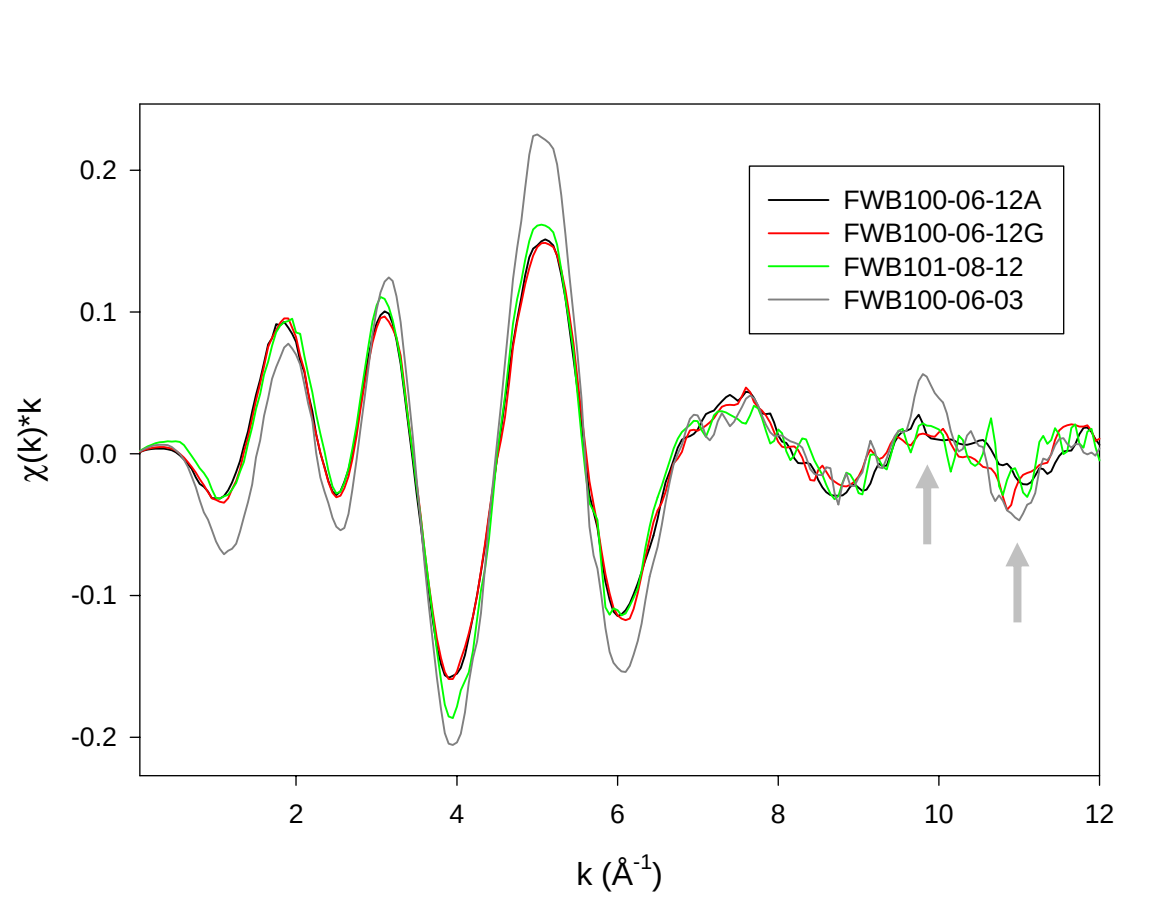


Area 3 and Area 1 samples





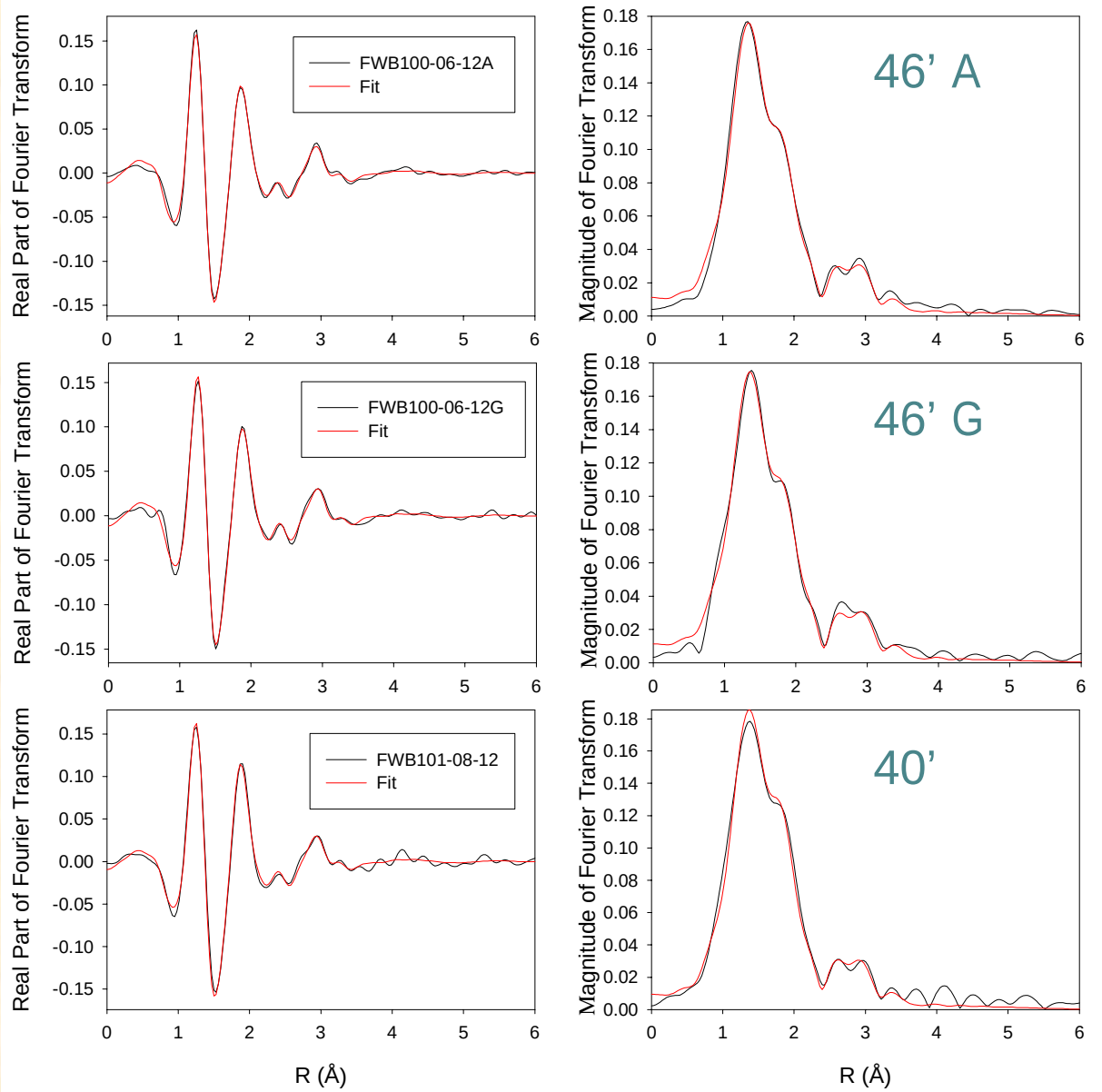




Comparison of EXAFS data Kelly, Kemner, et. al.

- **Data from 40' and 46' (black sandstone zone) are similar**
- **Data from 45' (gleyed shale zone) shows a signal from a heavy atom (U) by the increased amplitude in the oscillations at high wave number.**

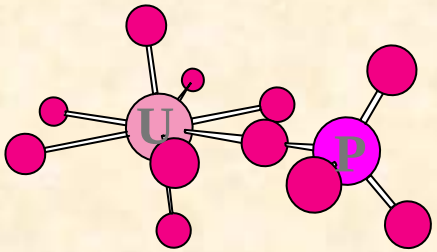
Fourier transform of data and fit to 40’ and 46’ data

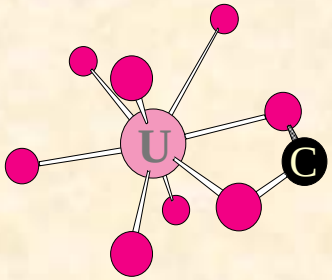


EXAFS Fit Results

Fit Results for phosphorus atoms bound to uranium

Depth	Sample	Number of P	Bond length (Å)	σ^2 ($x10^{-3}$ Å^2)
40’	FWB101-08-12	0.5 ± 0.7	3.611 ± 0.017	1.6 ± 3.7
46’ A	FWB100-06-12A	0.6 ± 0.3		
46’ G	FWB100-06-12G	0.6 ± 0.3		



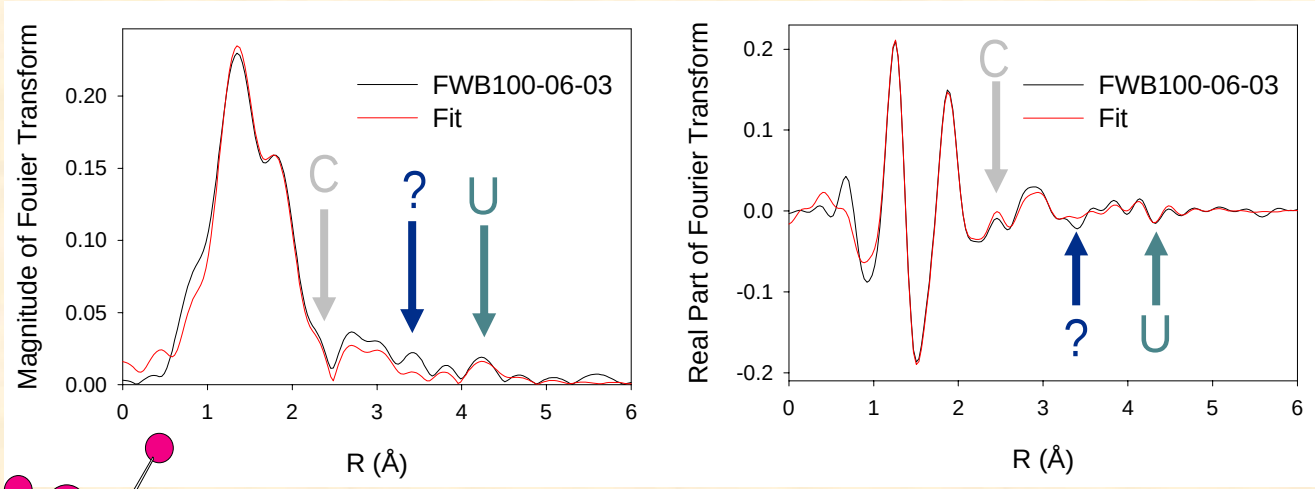


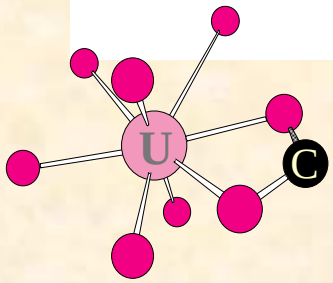
Fit Results for carbon atoms bound to uranium

Depth	Sample	Number of C	Bond length (Å)	σ^2 ($x10^{-3}$ Å^2)
40’	FWB101-08-12	1.0 ± 0.8	2.908 ± 0.012	0.0 ± 2.0
46’ A	FWB100-06-12A	0.9 ± 0.4		
46’ G	FWB100-06-12G	1.1 ± 0.4		

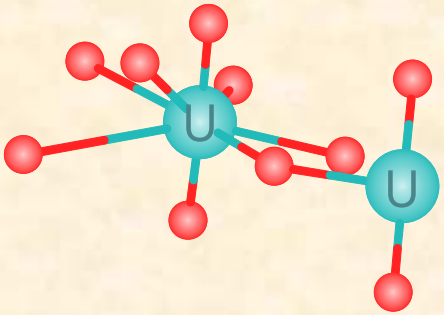
- U in the samples is mostly U(VI).
- Based on the number of carbon and phosphorus atoms there is a mixture of uranyl environments.
- U(VI) in all samples is coordinated by two tightly bound axial oxygen atoms and approximately 6 equatorial oxygen atoms.
- Data from 45 feet is different from data taken on samples from 40 and 46 feet. Indicating a different local atomic environment about the U atoms at 45 feet as compared to 40 and 46 feet.
- Model of the data at 46 feet (black sandstone zone) show that U is coordinated by bidentate carbon containing groups and monodentate phosphorous containing groups.

Current EXAFS Results for 45' deep gleyed weathered shale -FWB100-06-03





- **Preliminary model for the EXAFS data includes a U-C path and a U-U path.**
- **This model needs to be refined to account for additional signal in the data.**

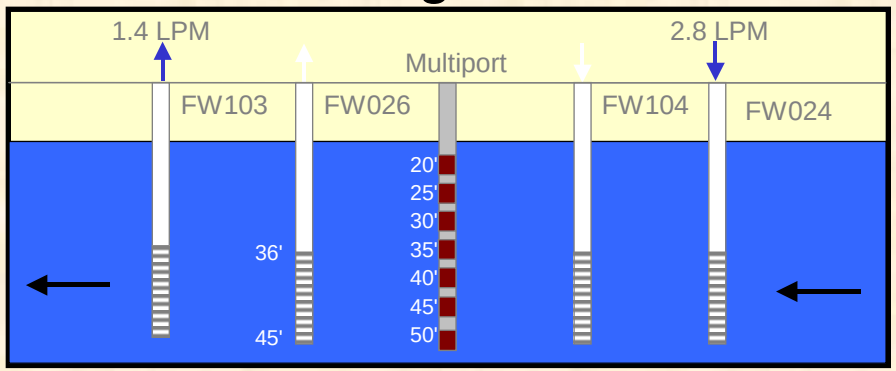


Geophysical Studies

- **Inductive electromagnetic (Geonics EM39) borehole profiling – ORNL (Beard, Gamey, Emonds, Sheehan)**
- **Seismic and Radar - LBNL (Hubbard et. al.)**
- **Geoprobe electrical conductivity probing**
- **Gamma counting - Thorium 232 finding**

Electromagnetic borehole logging

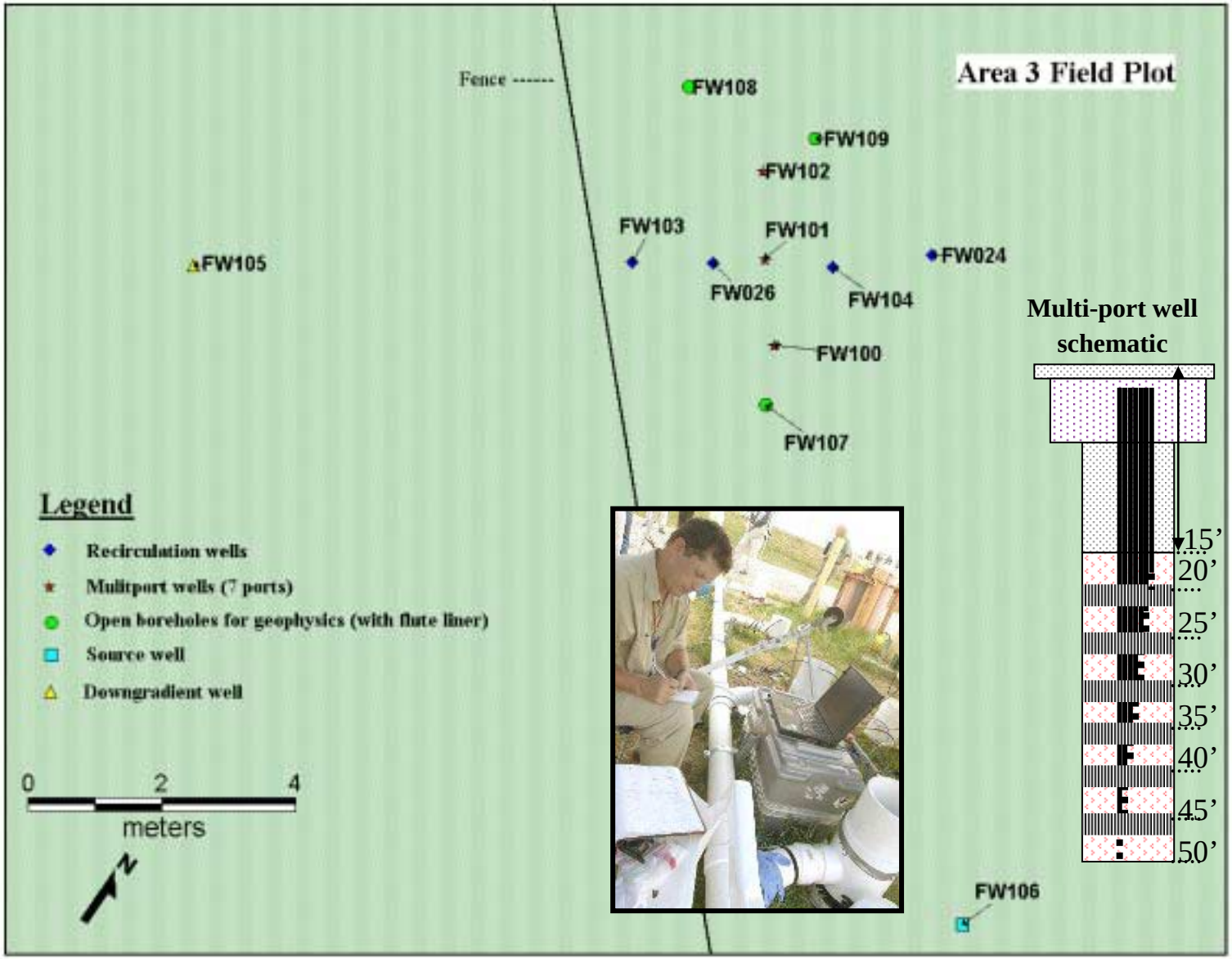
Area 3 flushing assessment



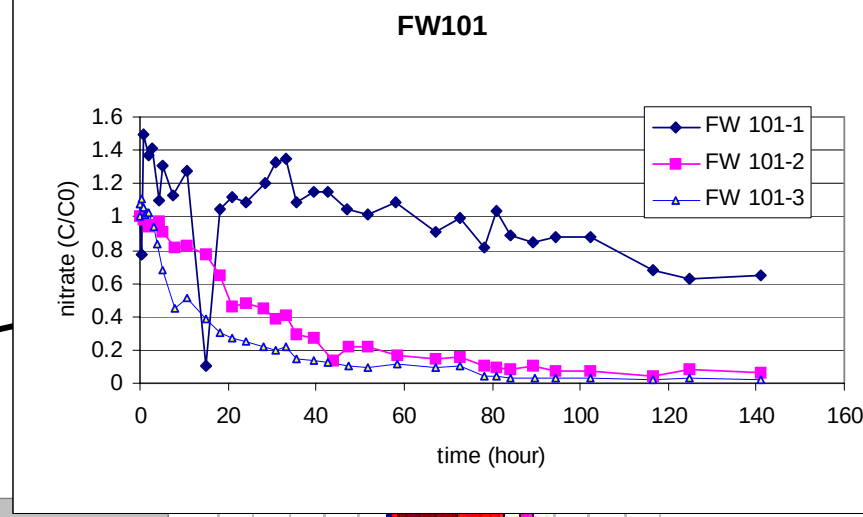
- Injection rates
  - FW024: 0-30 hrs 1.4 L/min, 30-143hrs 2.8 L/min
  - FW104 and FW026 76-143 hrs 0.7L/min
- Extraction rates
  - FW103 0-30 0.7 L/min, 30-143 hrs 1.4 L/min
- Samples from wells analyzed for nitrate with ion specific probe for comparison

- EM39 measures conductivity of the formation - 30cm radius
- Used to identify high conductivity clay zones and high TDS (high conductivity) groundwater
- Comparable to conductivity profiles collected with the Geoprobe
- Data collection
  - Profiles collected in Areas 1, 2, 3 and Background Area wells
  - Measured conductivity changes during flushing of Area 3 field plot with low pH, low conductivity tap water.

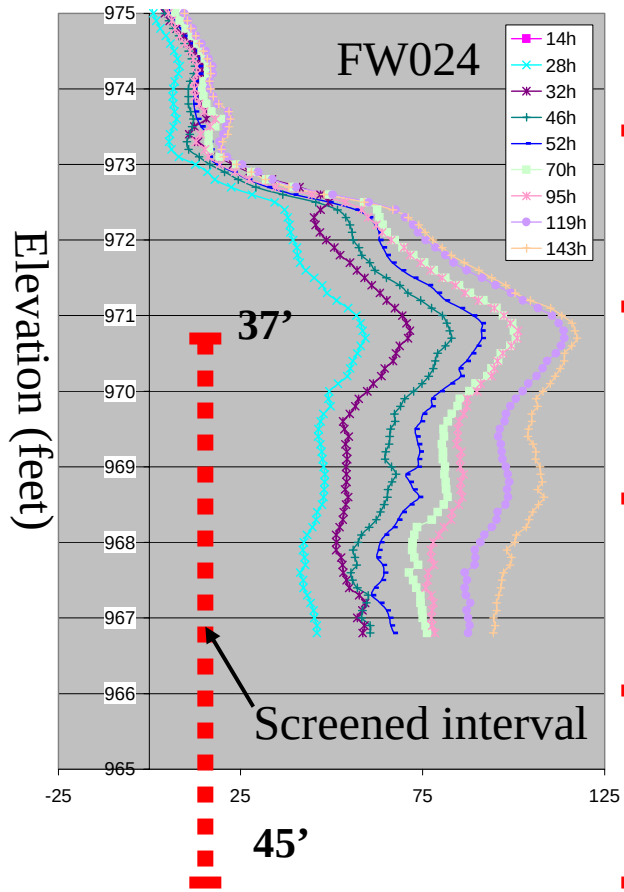
Monitoring locations at Area 3 plot

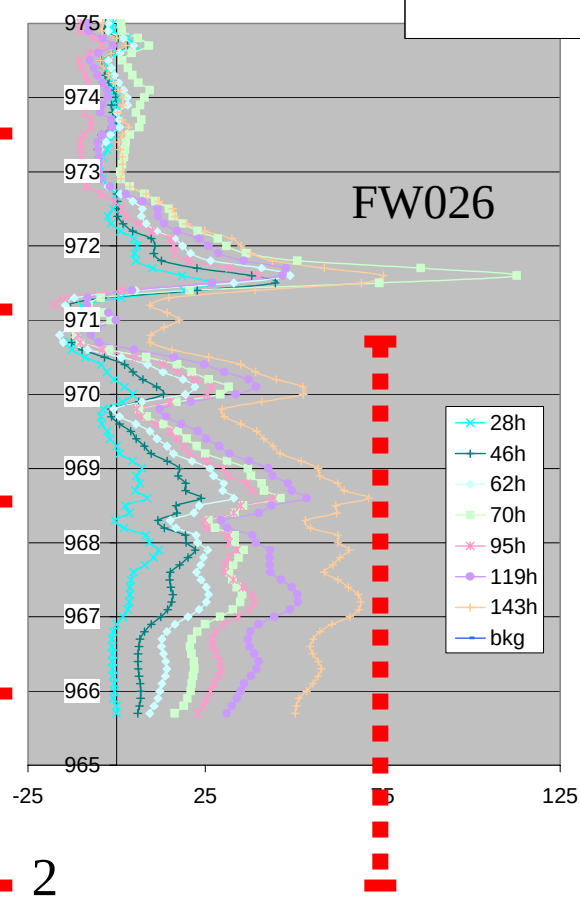


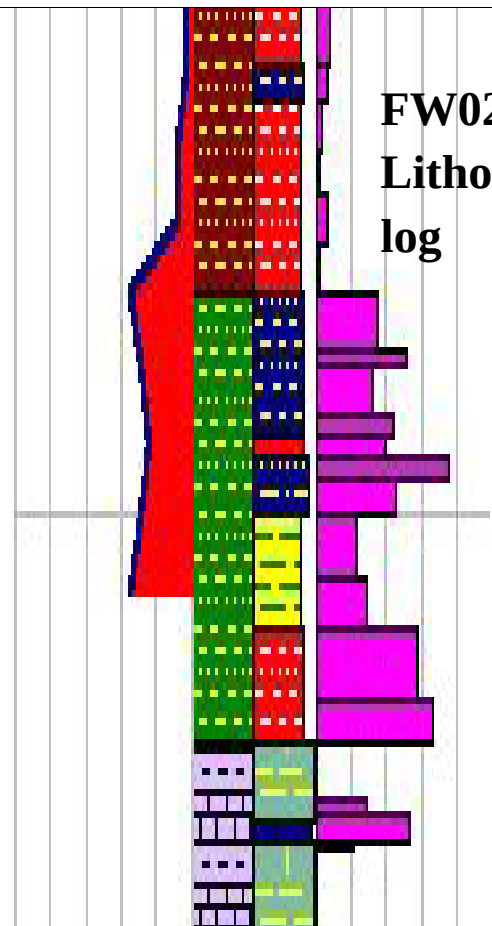
EM39 conductivity response comparison to nitrate changes in FW101 multiport



FW101 multiport

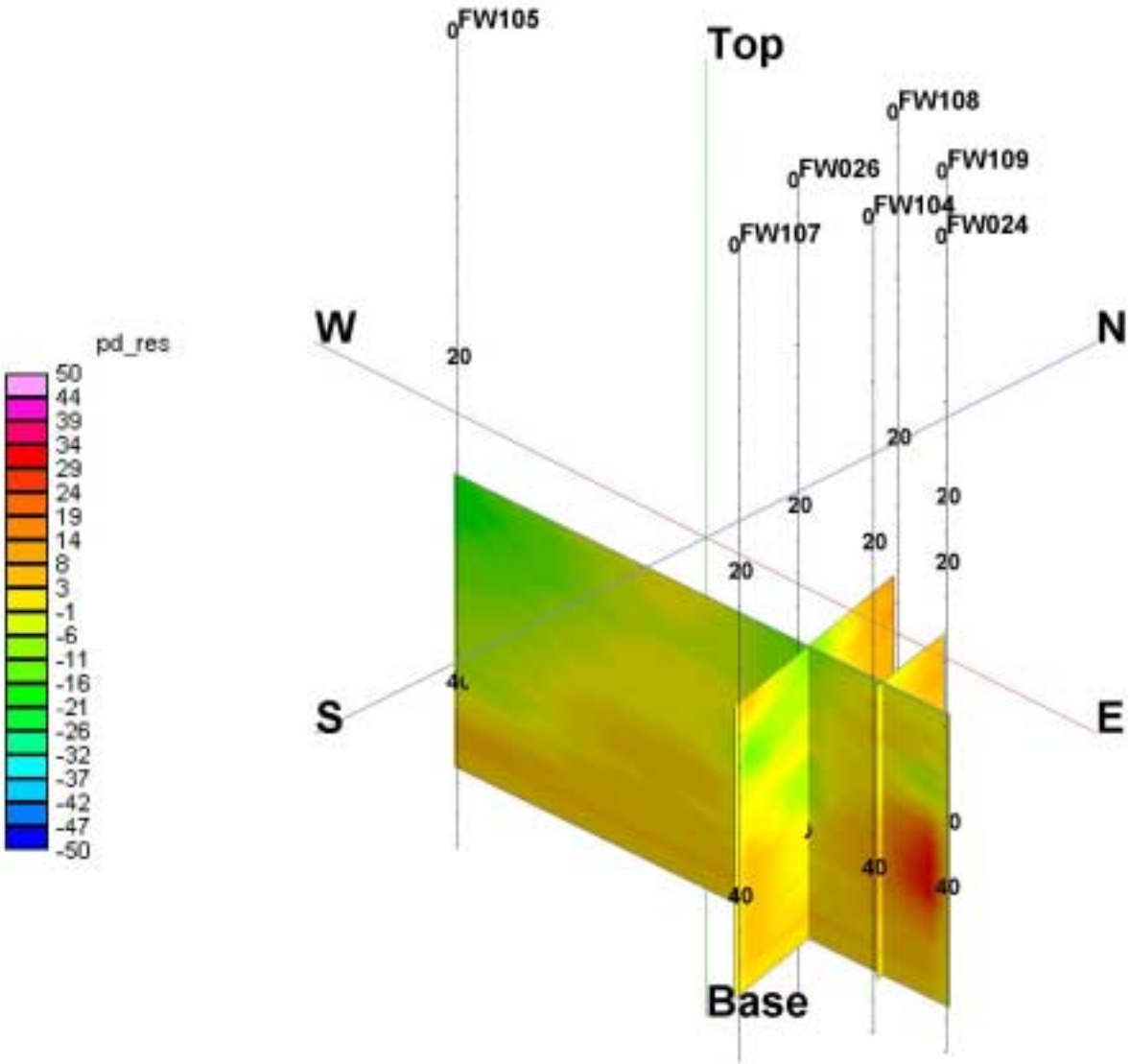






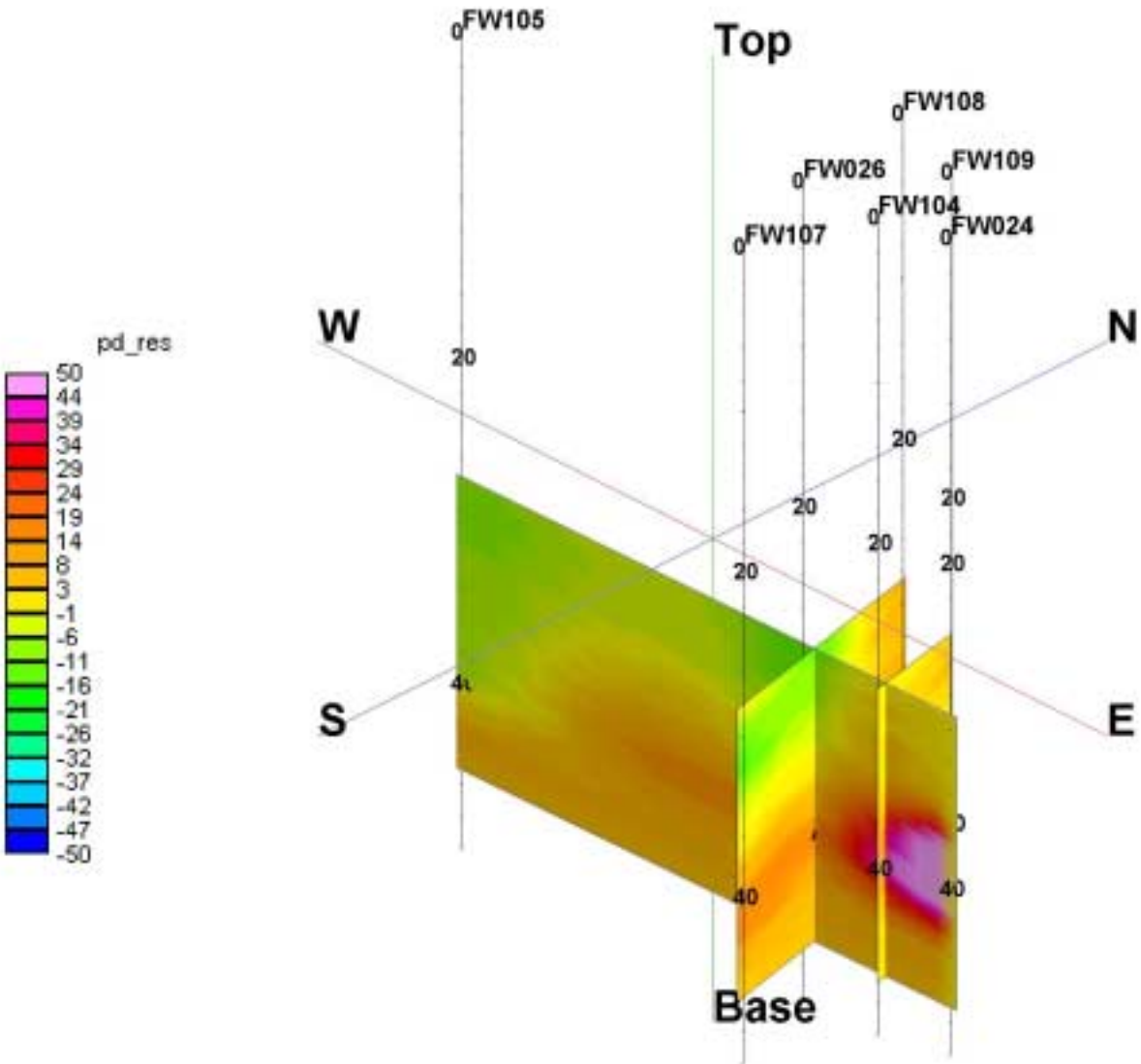
Percent increase in resistivity from t=0

Fence diagram



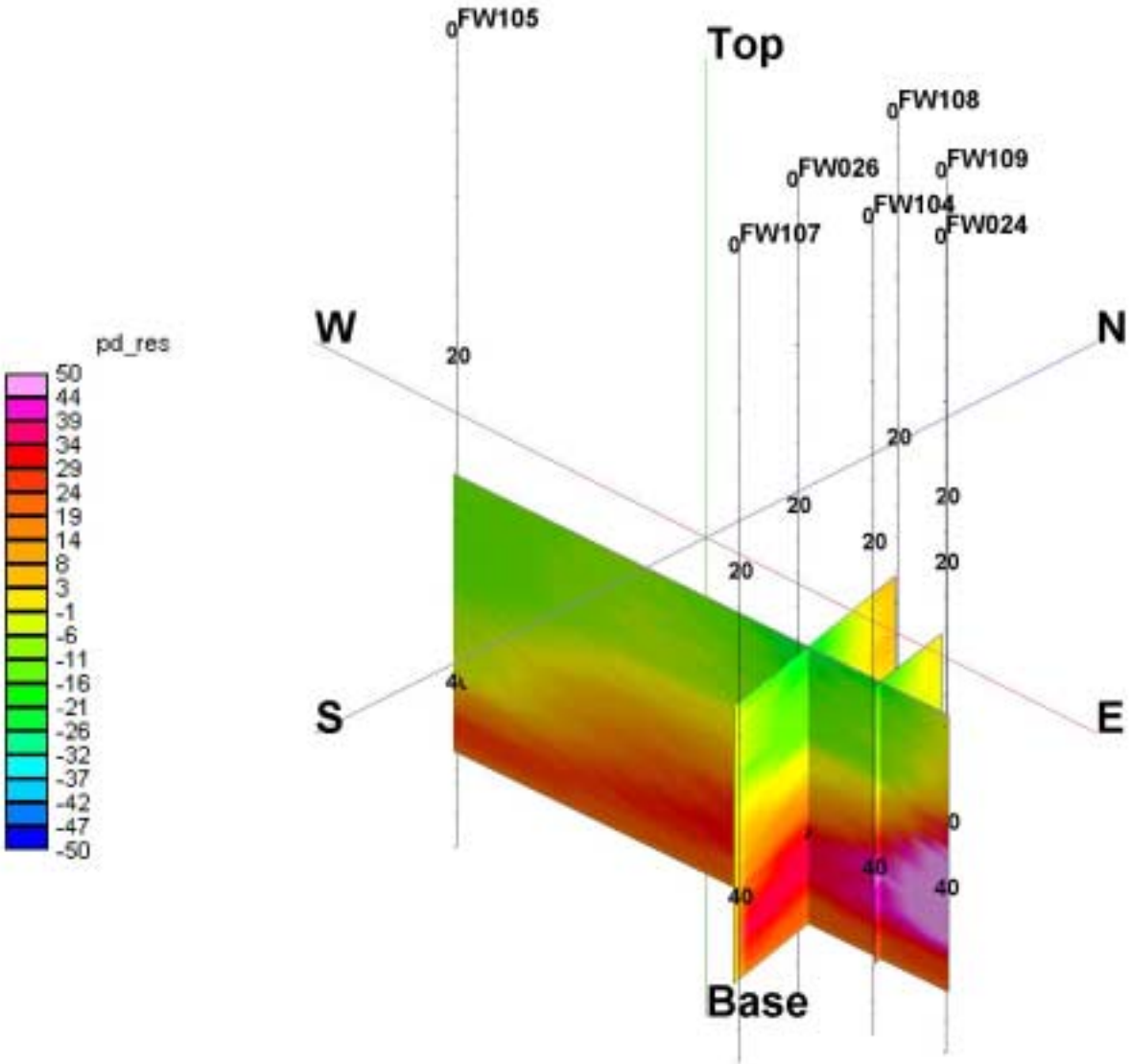
Percent change resistivity at t=14hrs

Fence diagram



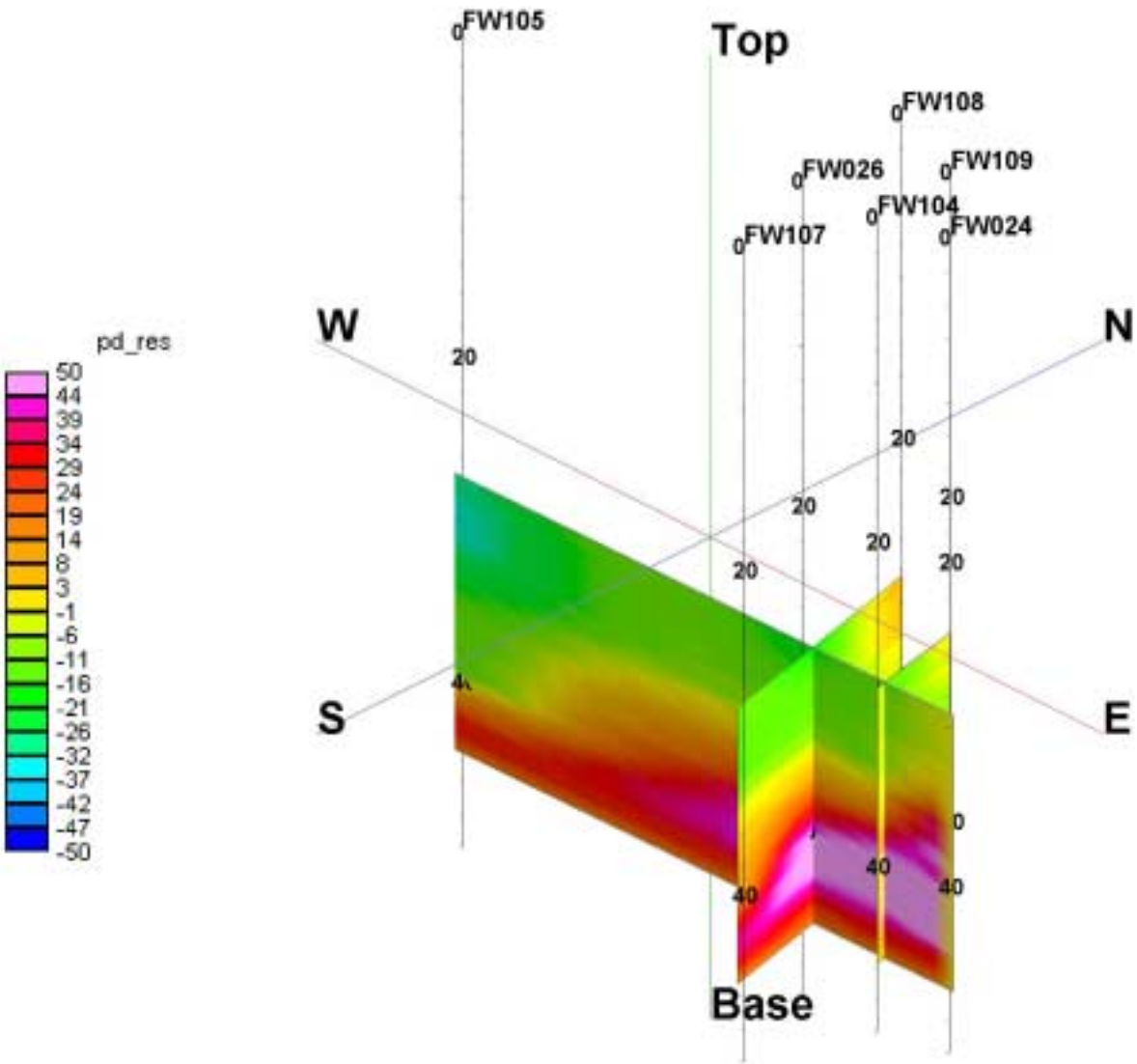
Percent change resistivity at t=46hrs

Fence diagram



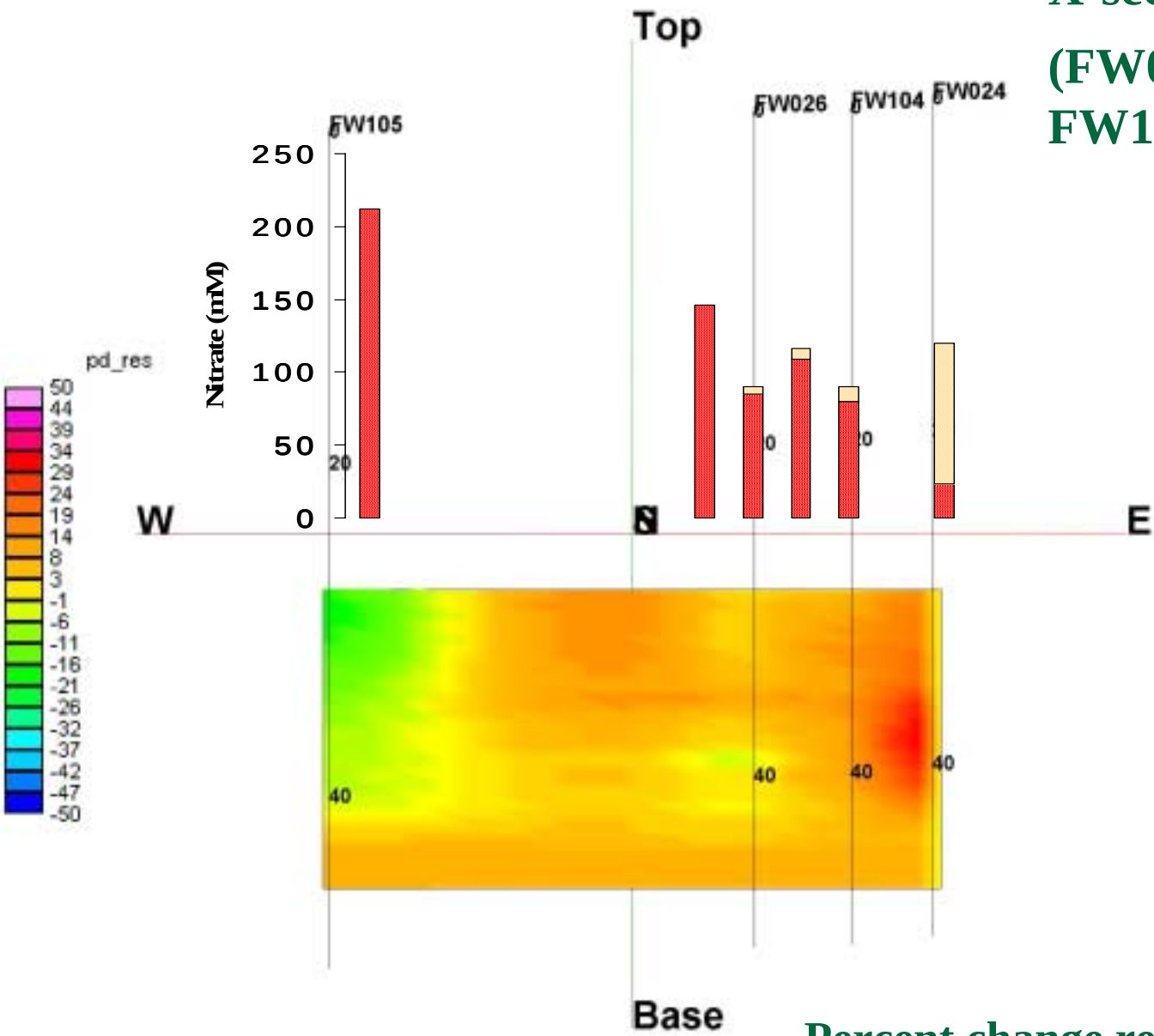
Percent change resistivity at t=119hrs

Fence diagram



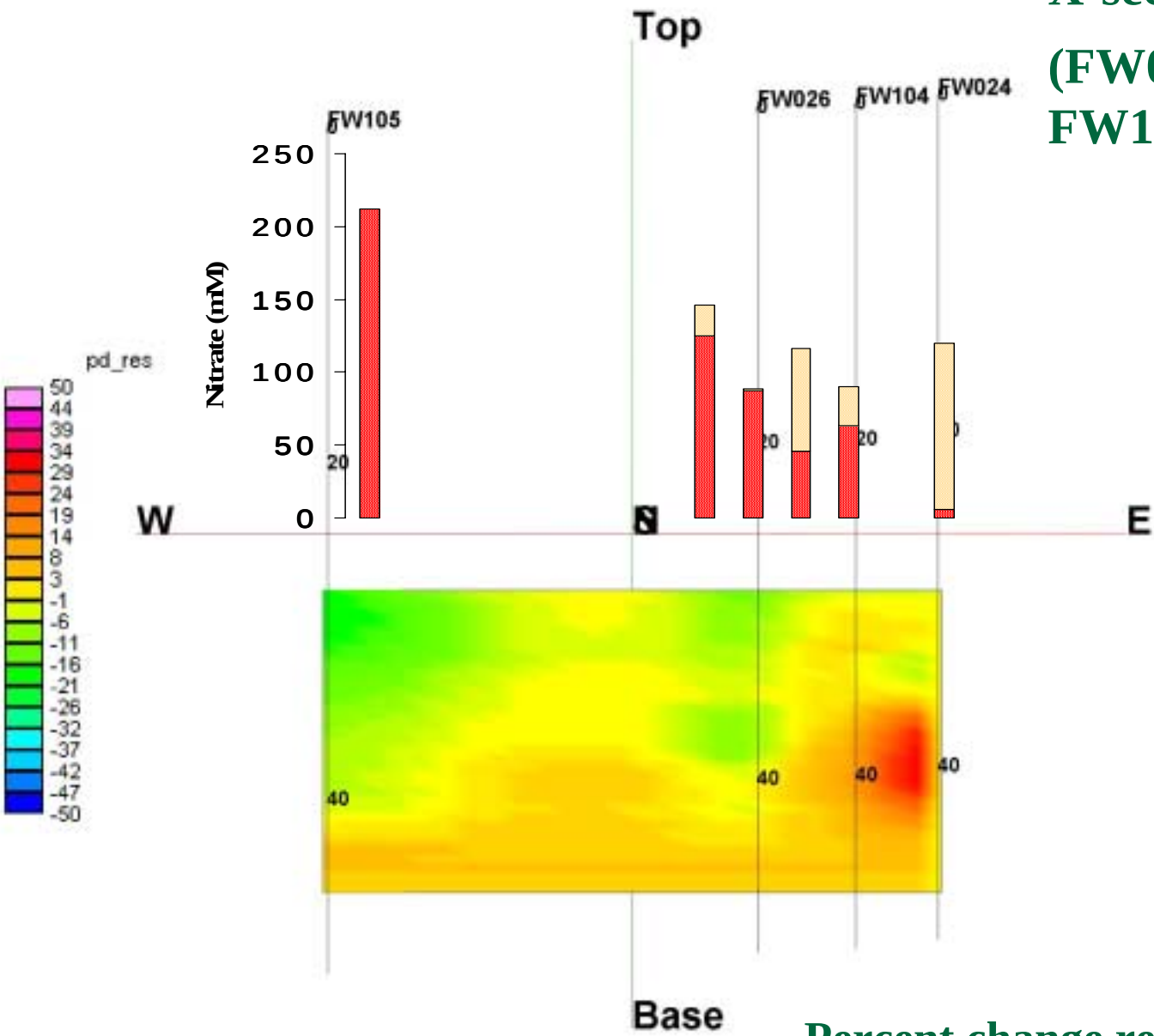
Percent change resistivity at t=143hrs

X-section parallel to flow (FW024-FW104-FW026-FW105)



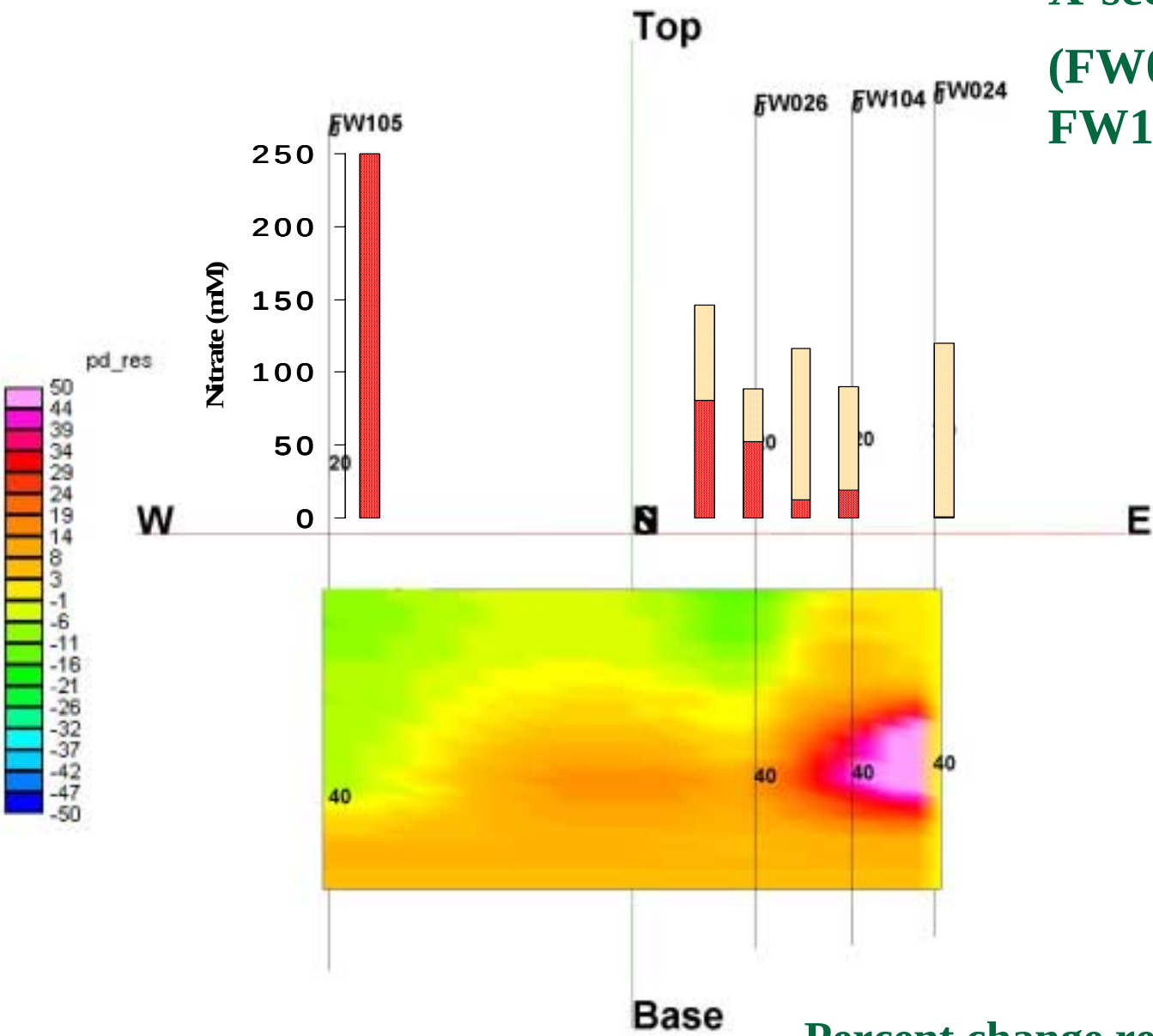
Percent change resistivity at t=3hrs

X-section parallel to flow (FW024-FW104-FW026-FW105)



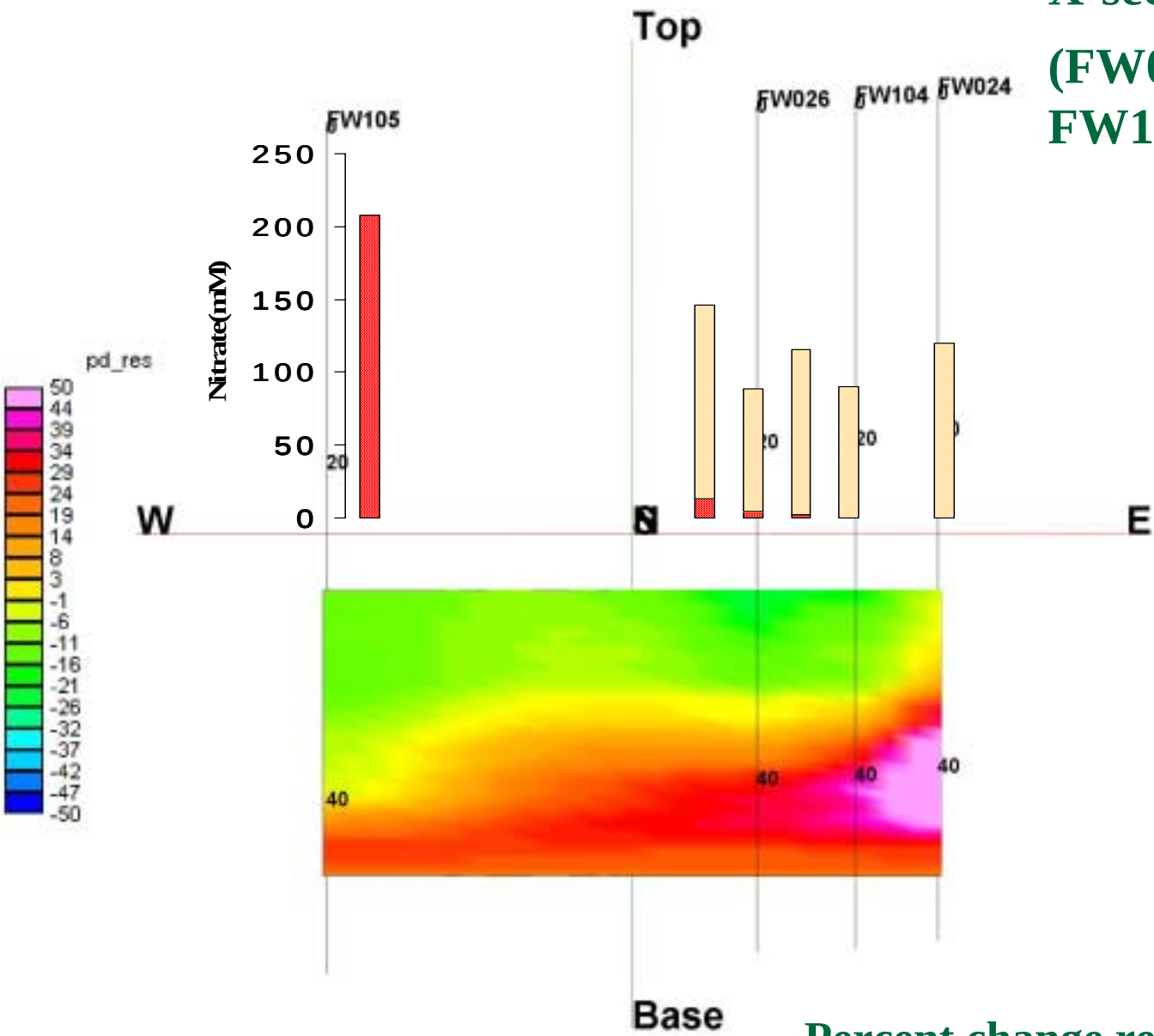
Percent change resistivity at t=14hrs

X-section parallel to flow (FW024-FW104-FW026-FW105)



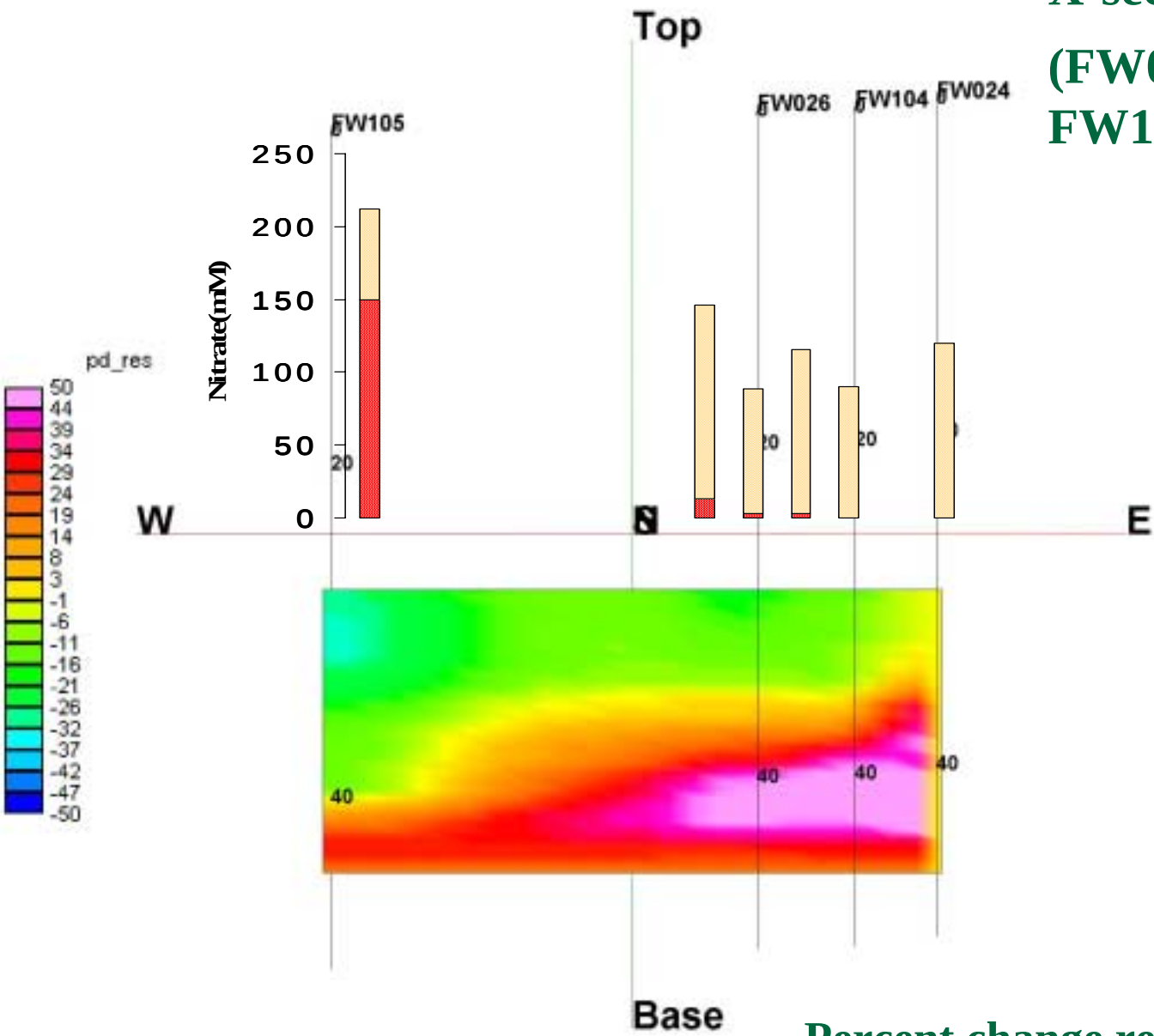
Percent change resistivity at t=46hrs

X-section parallel to flow (FW024-FW104-FW026-FW105)



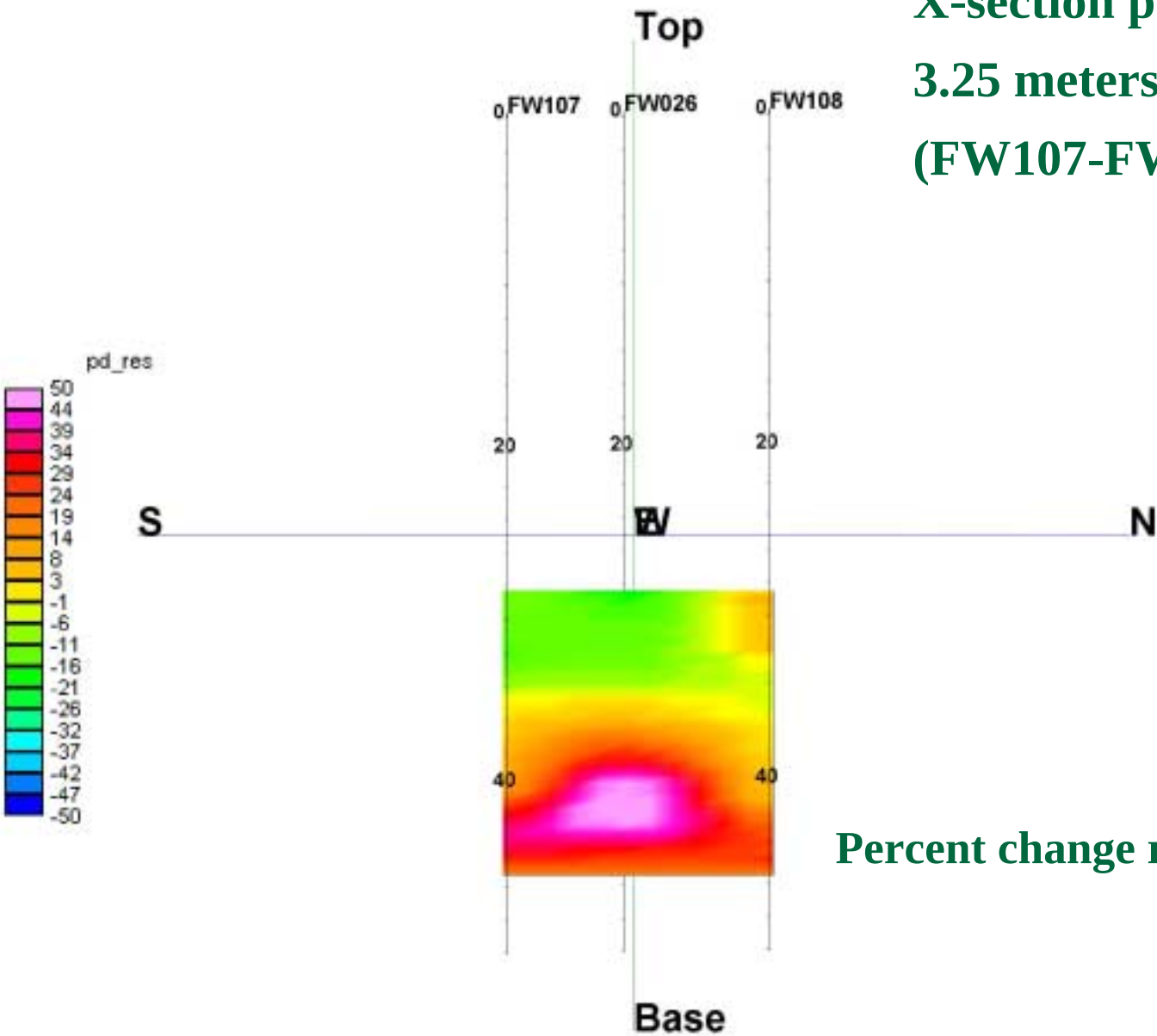
Percent change resistivity at t=119hrs

X-section parallel to flow (FW024-FW104-FW026-FW105)

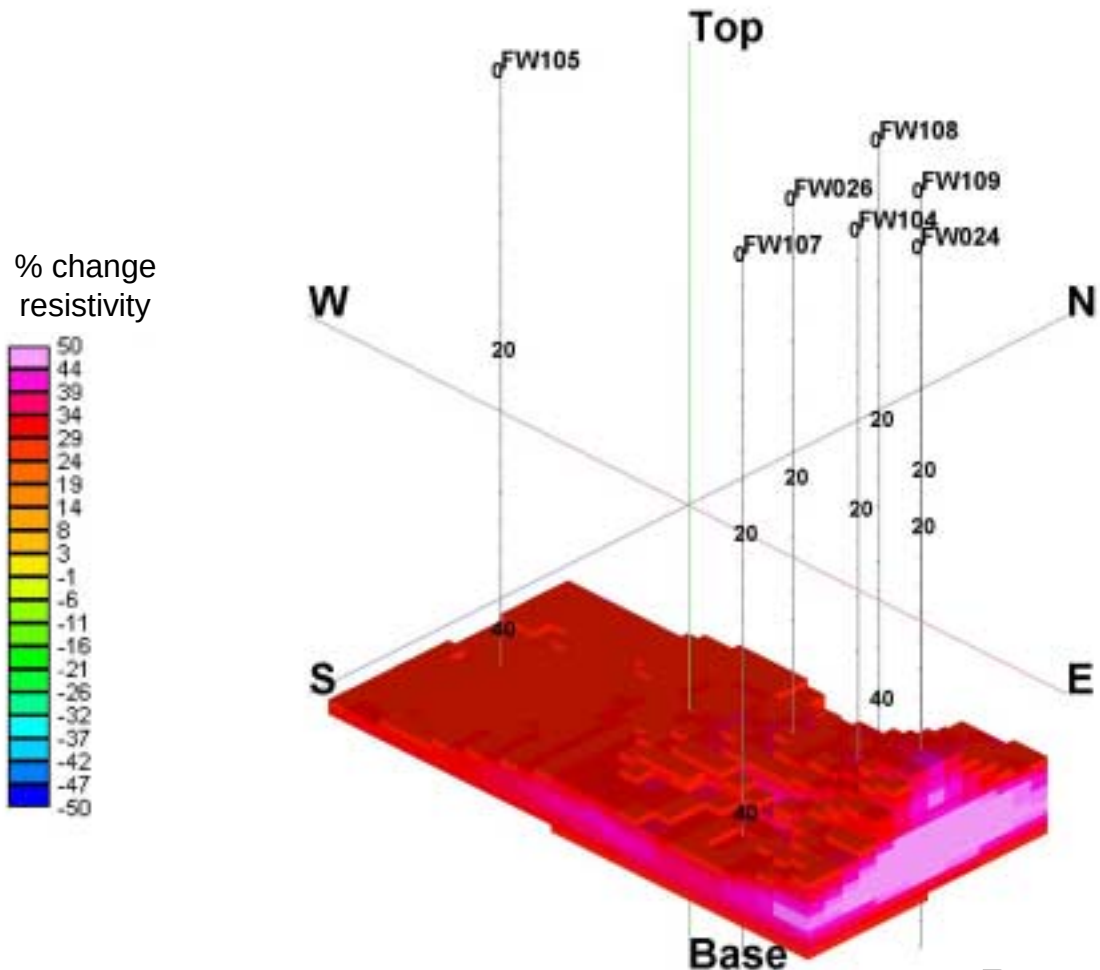


Percent change resistivity at t=143hrs

X-section perpendicular to flow 3.25 meters from injection well (FW107-FW026-FW108)



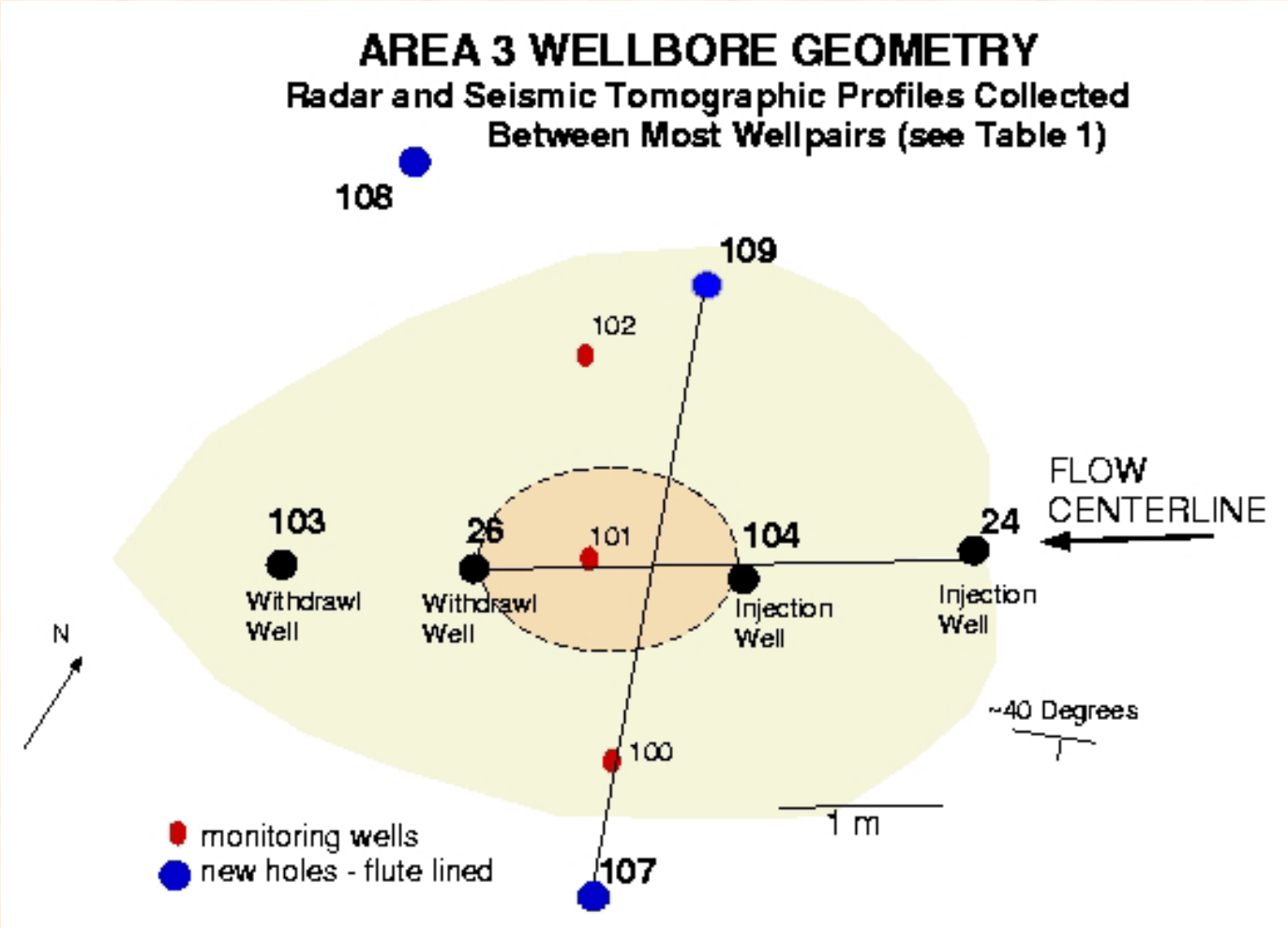
Percent change resistivity at t=143hrs

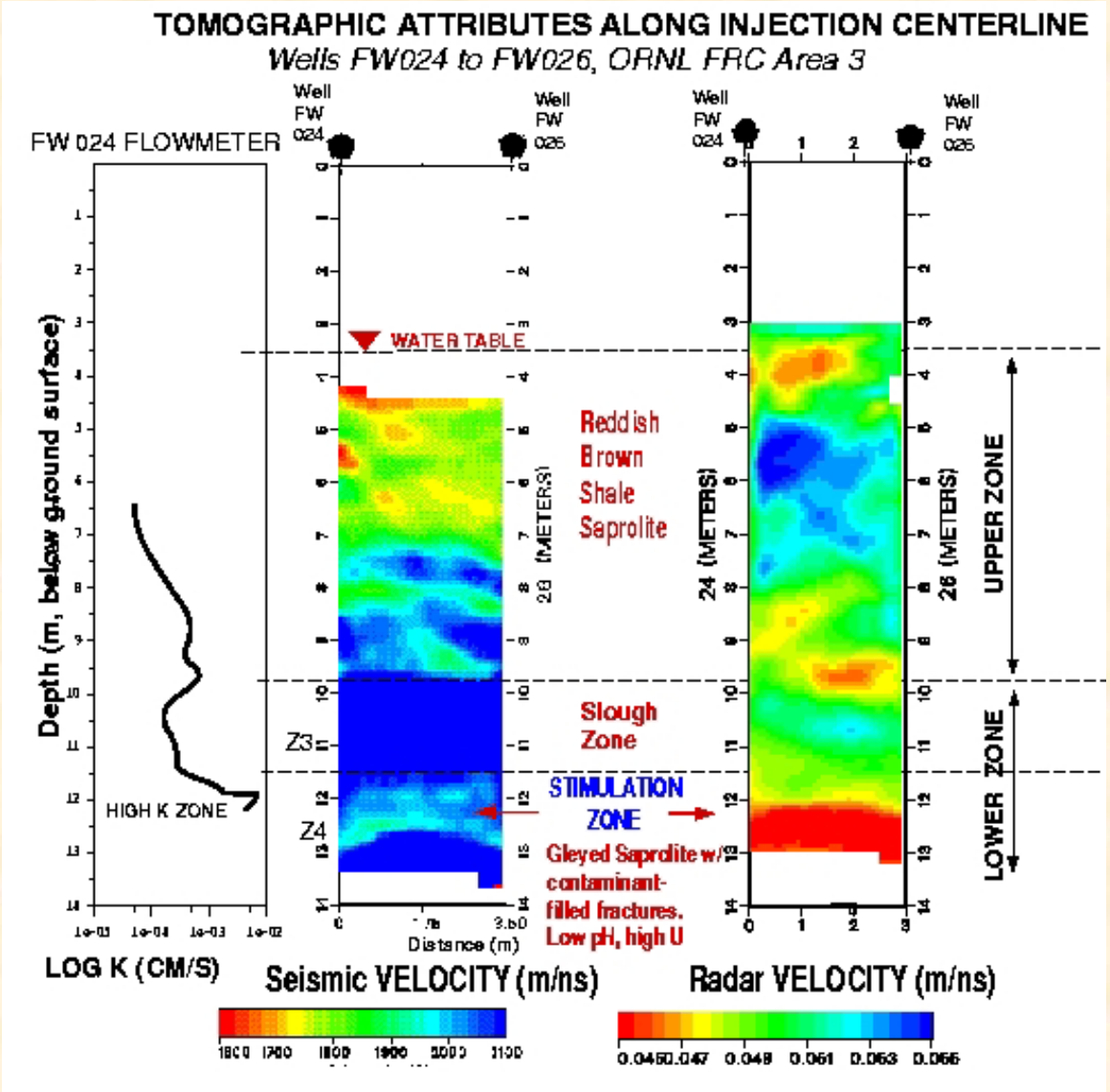


Time 143 hrs

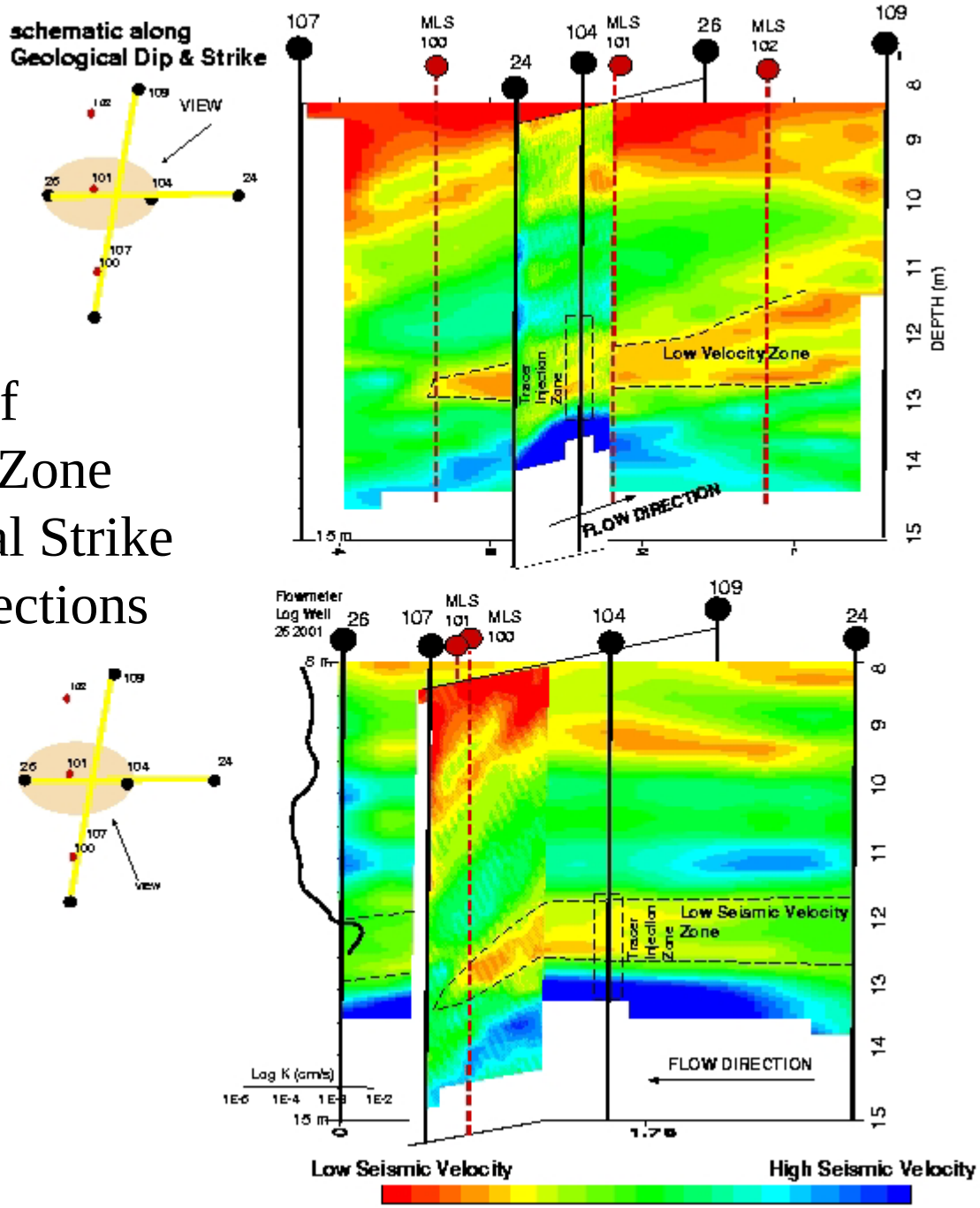
- Percent change in resistivity
- Iso-surface at +30%
- Average 16hrs between images

Radar and Seismic Tomographic Studies – Susan Hubbard et. al.

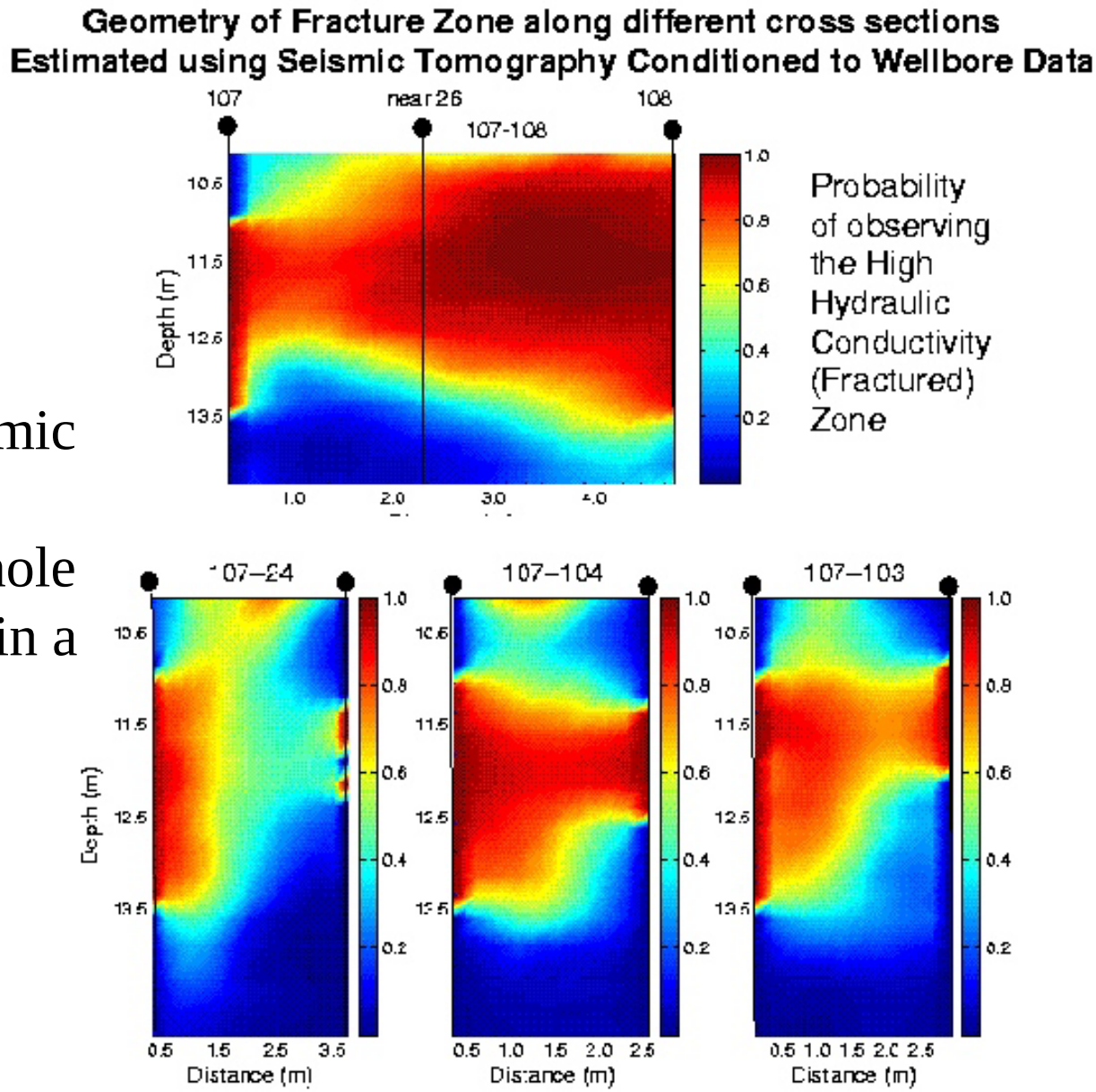



TOMOGRAPHIC ATTRIBUTES ALONG INJECTION CENTERLINE
Wells FW024 to FW026, ORNL FRC Area 3
FW 024 FLOWMETER
Well FW 024
Well FW 025
WATER TABLE
Reddish Brown Shale Saprolite
Slough Zone
STIMULATION ZONE
Gleyed Saprolite w/ contaminant-filled fractures. Low pH, high U
HIGH K ZONE
Z3
Z4
UPPER ZONE
LOWER ZONE
Depth (m, below ground surface)
24 (METERS)
26 (METERS)
Distance (m)
LOG K (CM/S)
Seismic VELOCITY (m/ns)
Radar VELOCITY (m/ns)

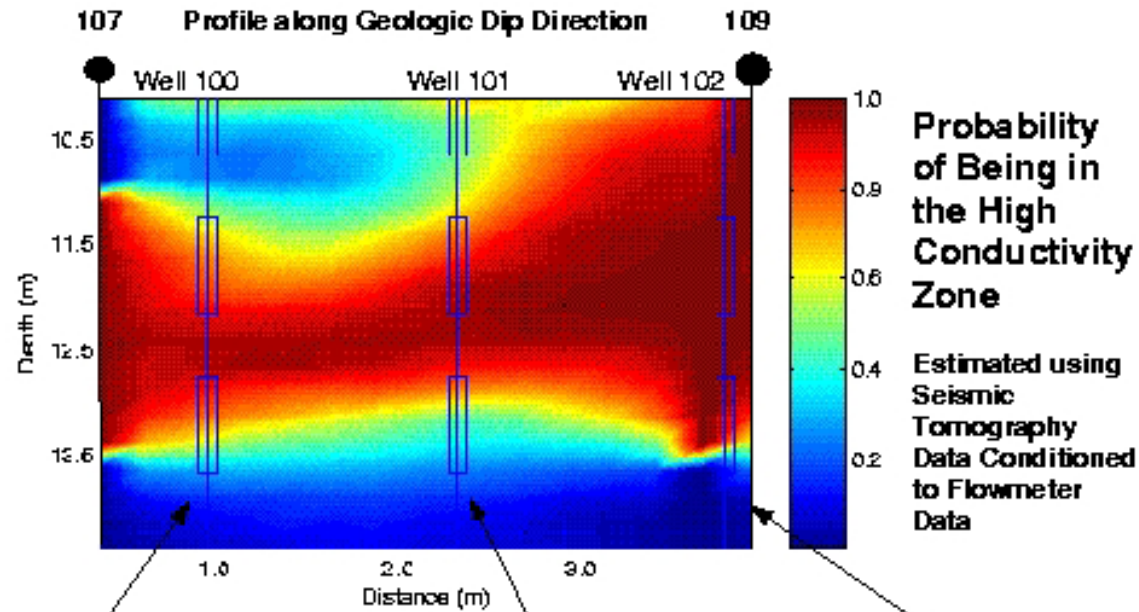
Geophysical Signatures of Stimulation Zone in Geological Strike and Dip Directions

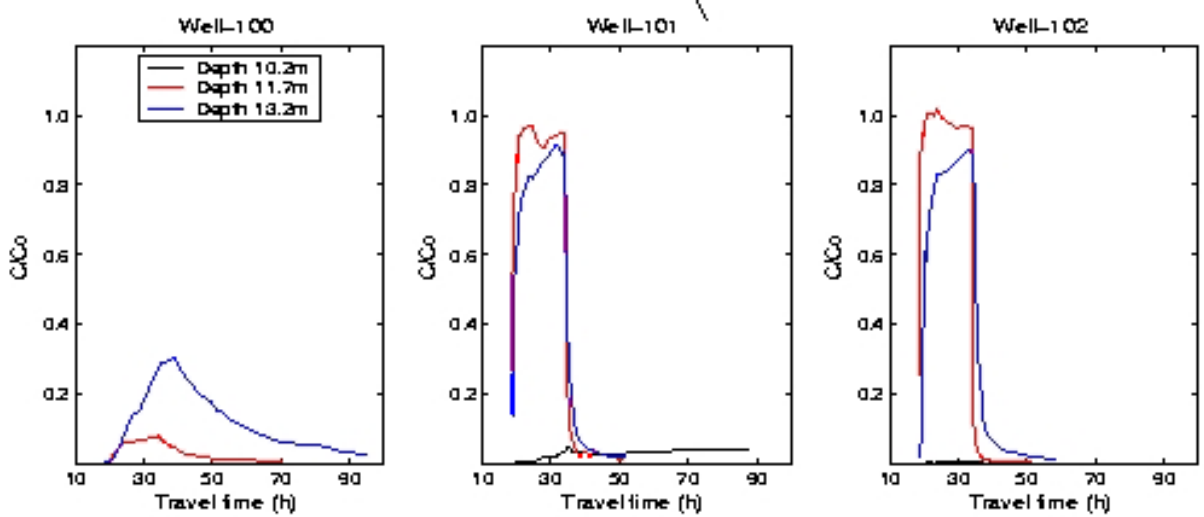


The probability of observing the high conductivity (fracture) zone was estimated using seismic tomographic data conditioned to borehole flowmeter data within a Bayesian approach.



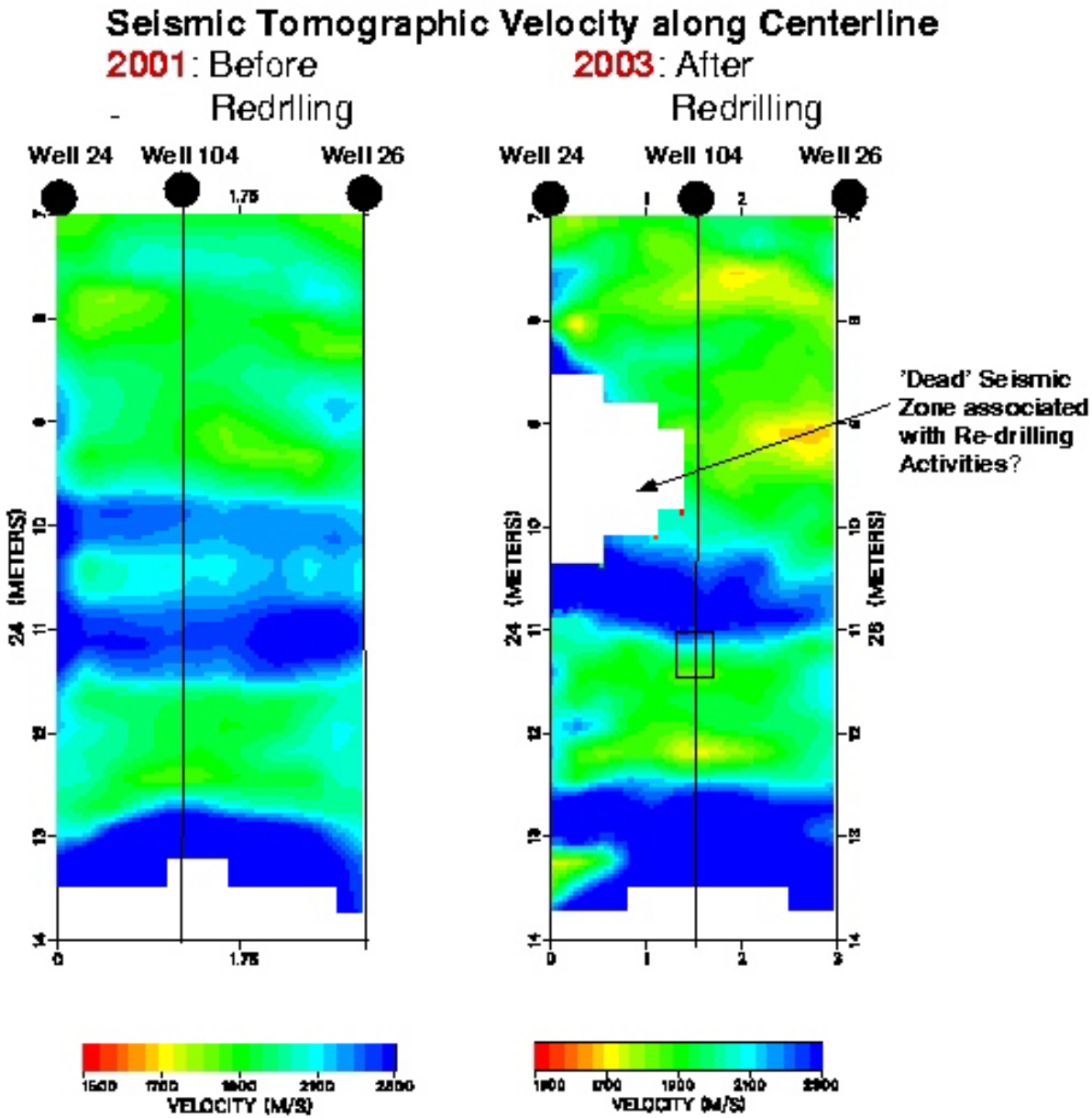
Fracture zonation, estimated using the geophysical data, appears to correlate well with the bromide tracer transport direction



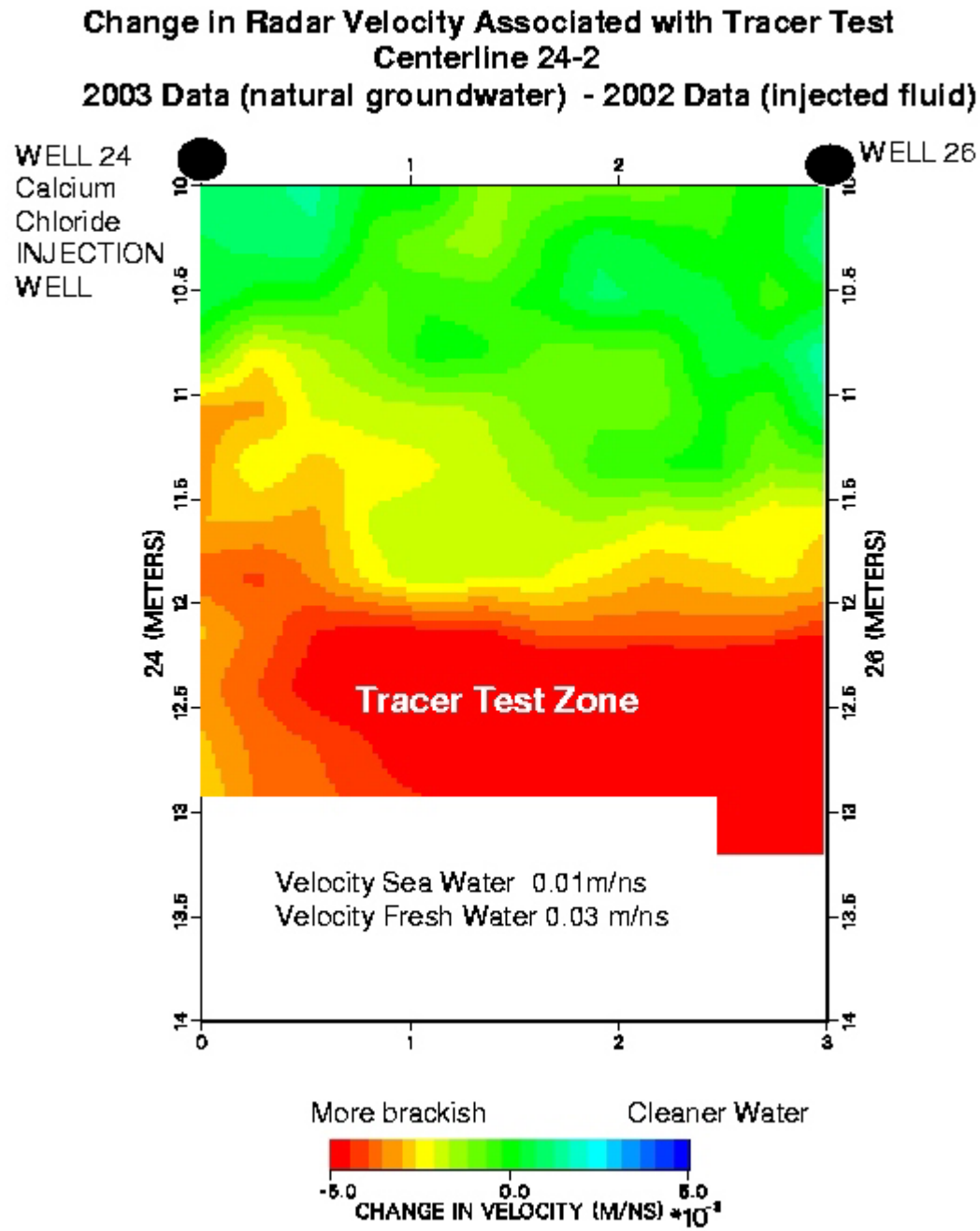


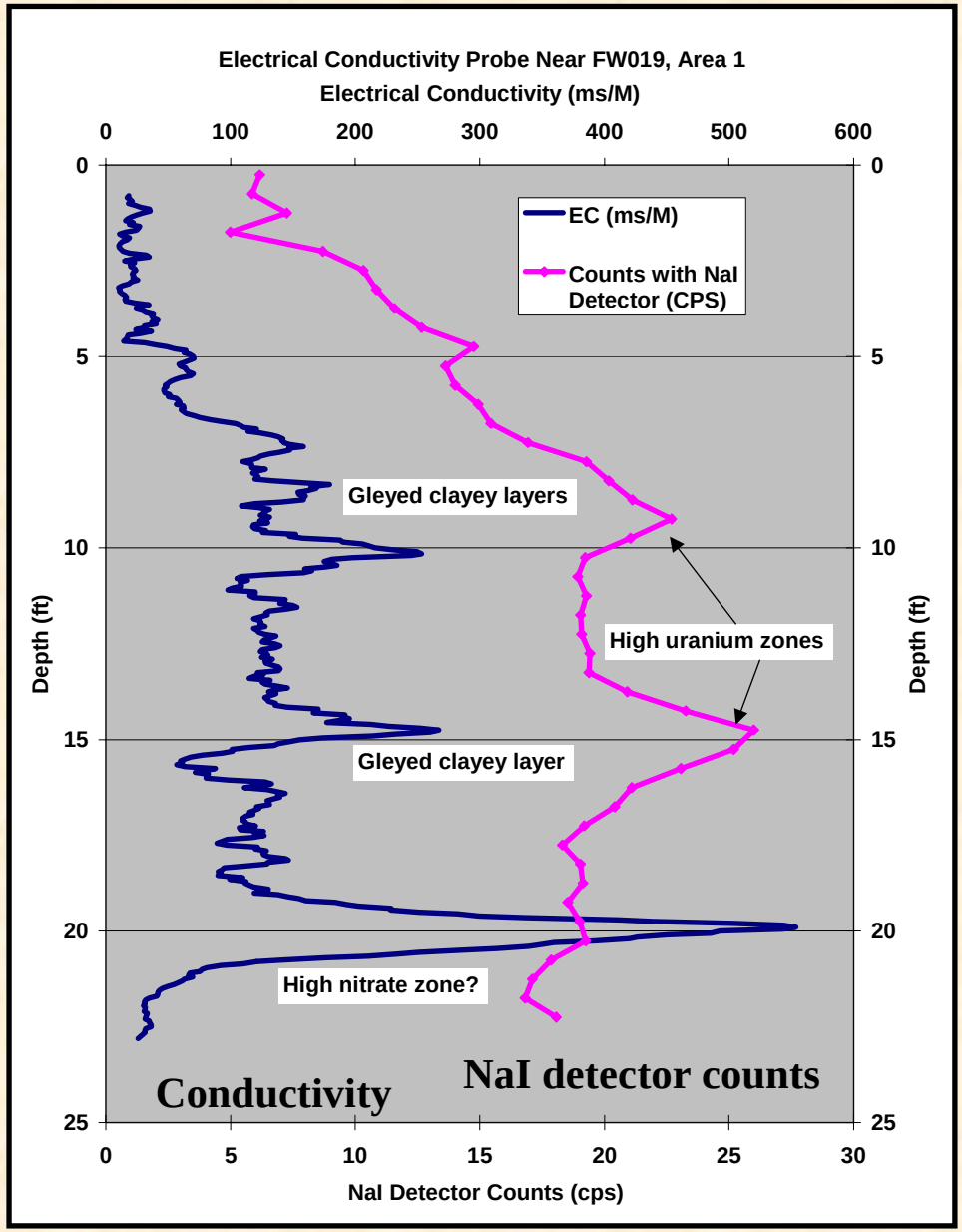
Tracer Breakthrough at 3 Multi-Level Samplers along Geologic Dip Direction

Seismic tomographic data are sensitive to Subsurface disturbances. In this example, the seismic data illustrate a zone of disturbance that was detected after re-drilling activities.



Radar tomographic data are very sensitive to the pore fluid. In this example, radar velocity variations were detected in the injection zone after a tracer test had been performed due to the differences in ionic strength of the injectate and natural groundwater.



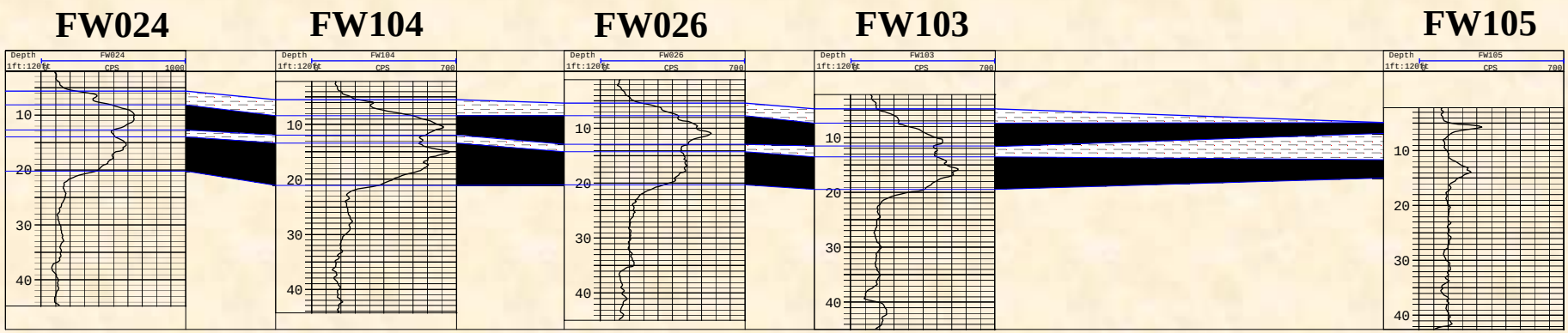


Electrical Conductivity Probing with FRC Geoprobe

- Useful for mapping stratigraphy and high U zones

Borehole gamma logging

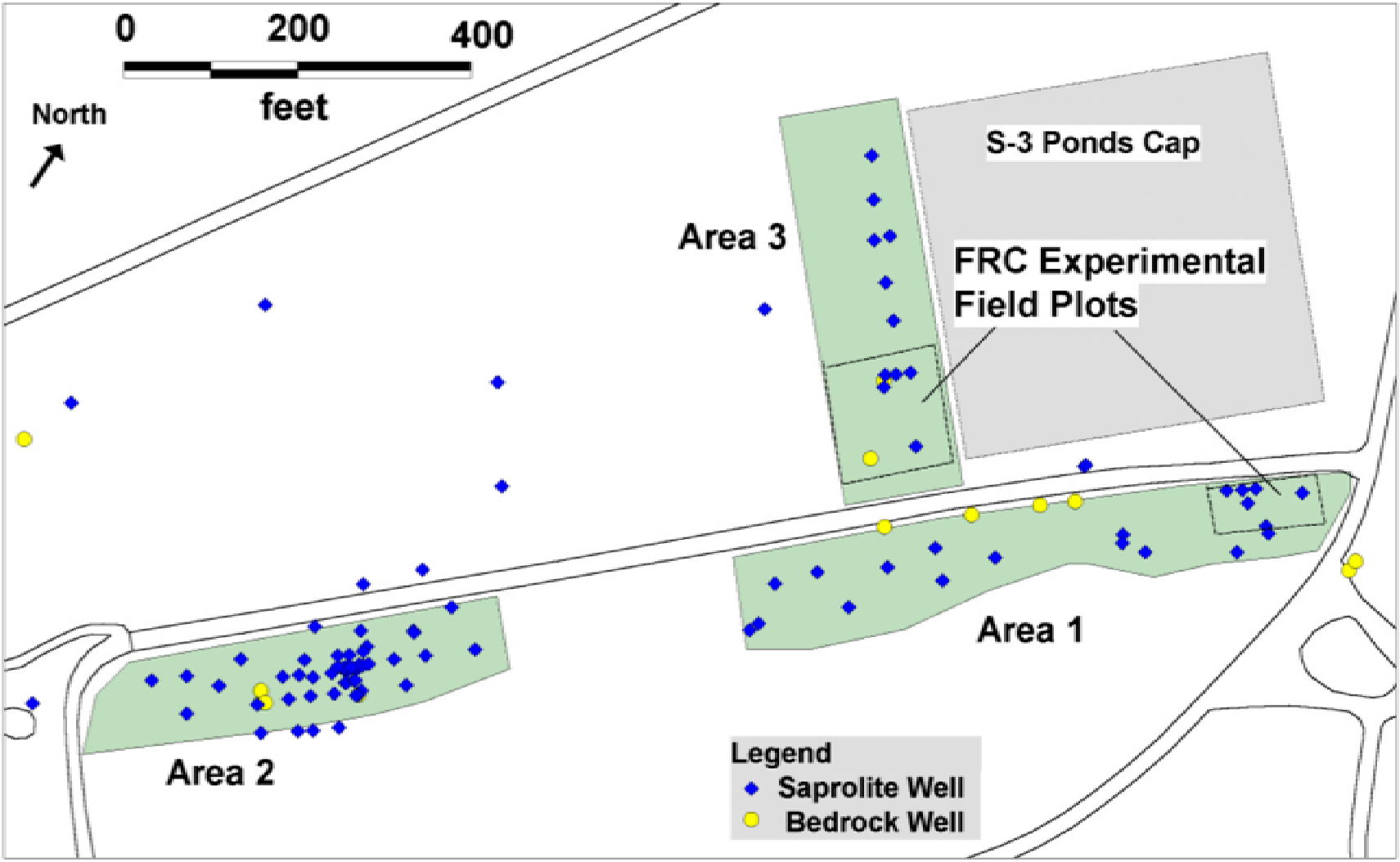
- High gamma at FRC generally is associated with high U content in sediment
- High gamma in shallow zone at Area 3 transect but sediment has a low U content
- Analysis with high resolution gamma spectroscopy shows that the high gamma is related to the presence of ^{232}Th in clays



Upcoming Field Work

- **Characterization for FRC expansion to the west and east of the S-3 Ponds**
- **Continuation of Area 2 field plot characterization**
  - **Coring and well installation**
  - **Geochemical and microbial studies on groundwater and sediment**
  - **Hydraulic studies**
  - **Geophysics**
- **More detailed characterization of Background Area**
- **Collection of cores from Areas 1, 2, and 3, and Background Area**

Field Plots in Contaminated Area



FRC Contributors

- Sample collection, processing, shipping, and analysis – Tonia Mehlhorn, Barry Kinsall, Kenneth Lowe, Mary Anna Bogle, George Houser, Steve Childs, Kirk Hyder, and Norman Farrow,
- Geophysics - Bill Doll, Les Beard, Jeff Gamey, and Jacob Sheehan
- Soil Characterization - Debra Phillips and Yul Roh
- Database and website - Craig Brandt, and Susan Holladay
- Regulatory issues - Harry Quarles and Monty Ross
- Geochemistry - Scott Brooks and Philip Jardine
- Microbiology - Susan Pfiffner
- Humics- Baohua Gu
- BASIC - Amy Wolfe
- Administrative - Lynda Campbell
- Stanford and ORNL – Craig Criddle, Phil Jardine, Wei-Min Wu, Peter Kitanidis, Mike Fienen, and Susan Hubbard (geophysics)
- OSU/OU – Jack Istok and Lee Krumholz
- PNNL/ORNL/UA – Tim Scheibe, Scott Brooks, Eric Roden
- FRRP – Terry Hazen et. al.
- XAFS – Ken Kemner, Shelly Kelly (ANL)
- Coupons – David White and Aaron Peacock (UT) and David Cummings and Gill Geesey (INEL)