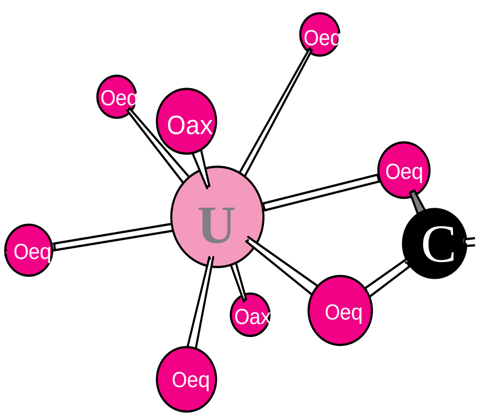
Geochemical/Geophysical Characterization Working Group

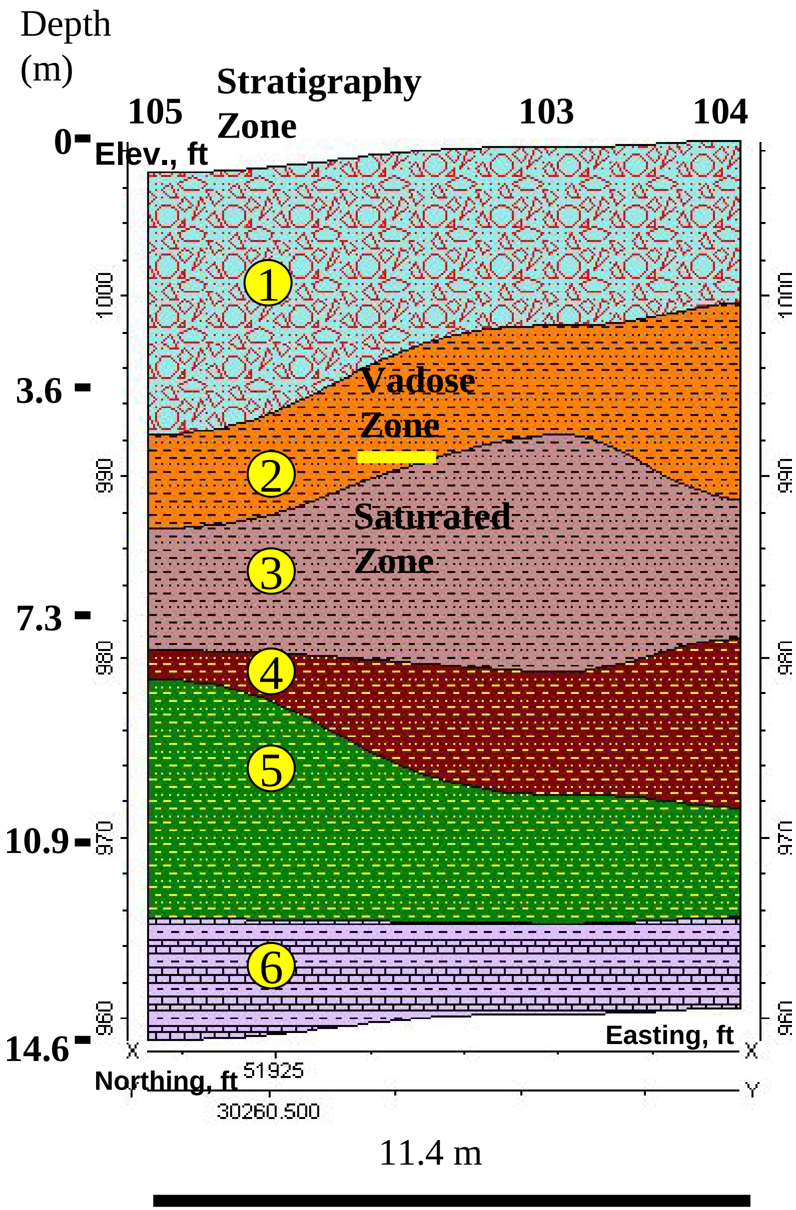
Research Briefs and Coordination

NABIR FRC Workshop
September 22-24, 2003



Stratigraphic and Lithologic Characterization

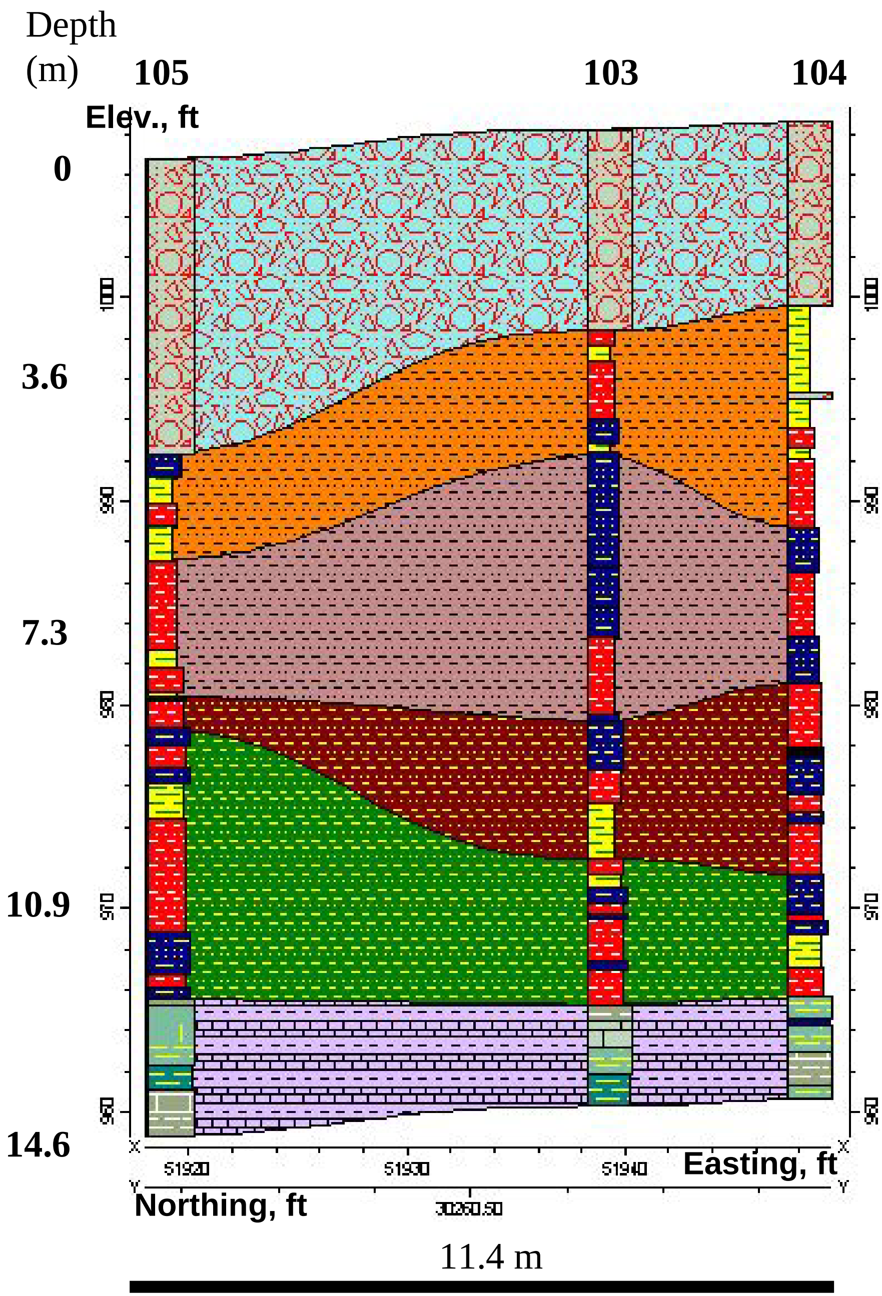
General Description and Interpolation of the Stratigraphy between the Cores

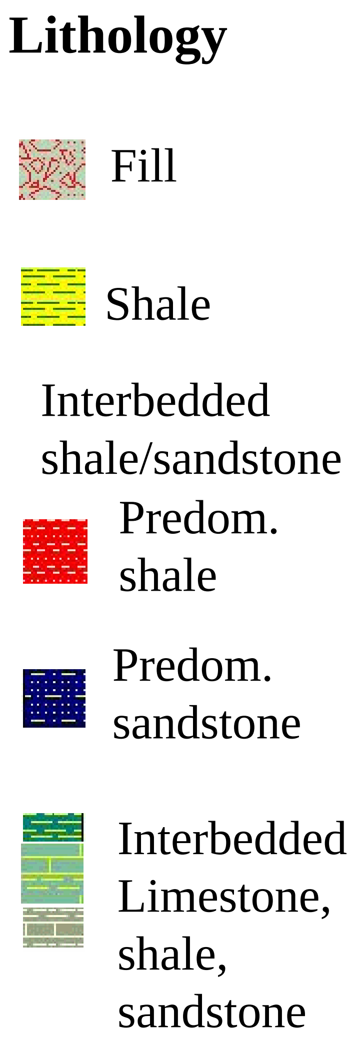


General Stratigraphy	Zone	Rock	Major Color	Moist Consistence
Fill	1	Mixture of limestone, soil and saprolite		
Interbedded Shale and Sandstone Saprolite	2	Shale	7.5YR 5/6	V. friable-friable
		Sandstone	10YR 5/4	V. friable-firm
	3	Shale	7.5YR 5/6, 2.5Y 5/4	V. friable-friable
		Sandstone	10YR 4/4	V. friable-firm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

Phillips and Watson, 2003

General Description of the Lithology of the Cores



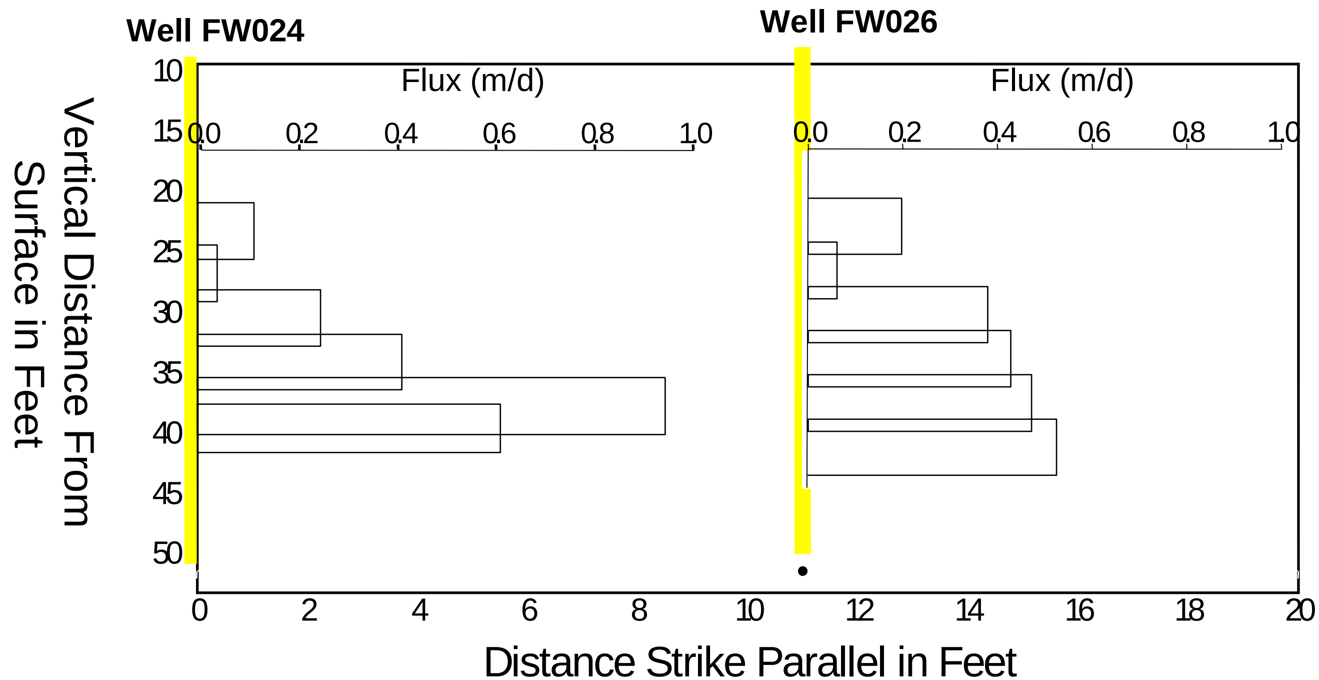


Phillips and Watson, 2003

Hydrologic Characterization

Groundwater flux

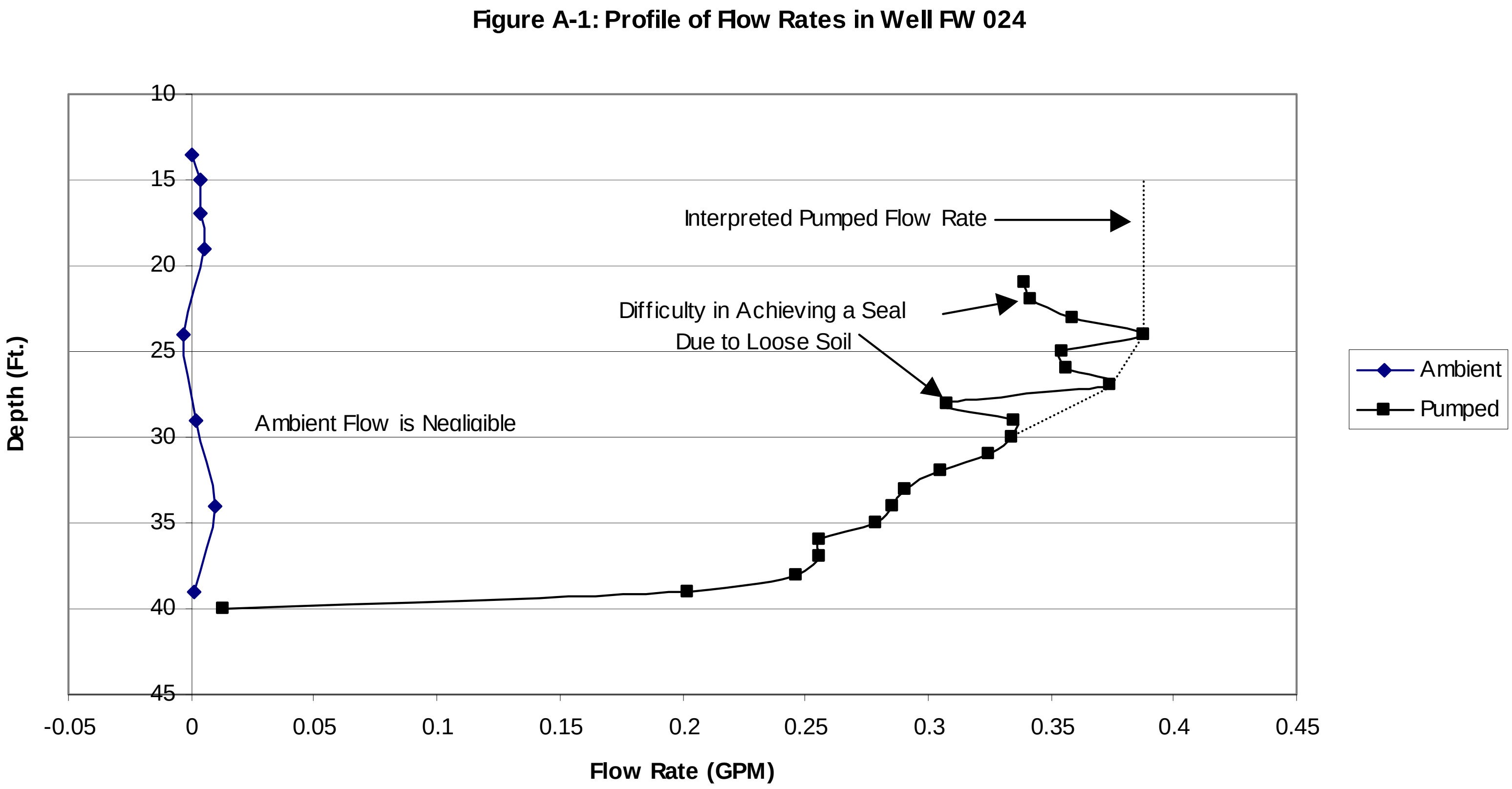
Groundwater Flux at FRC Area 3



- **Point dilution technique for estimating groundwater flux as a function of depth.**

Mehlhorn et al., 2003

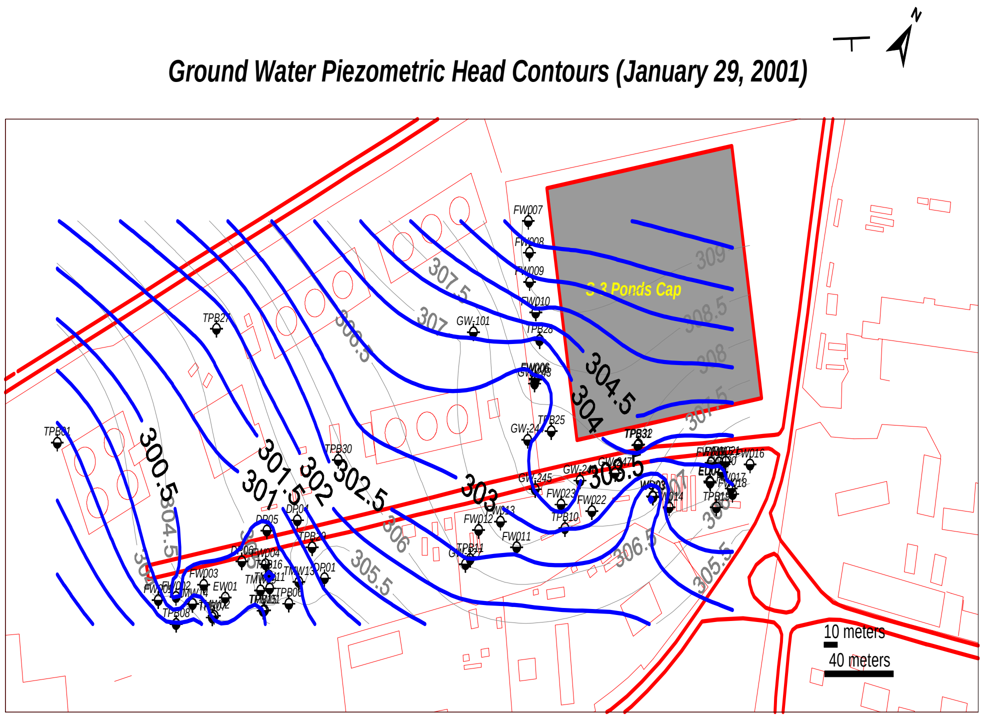
Borehole flowmeter for estimating hydraulic conductivity as a function of depth

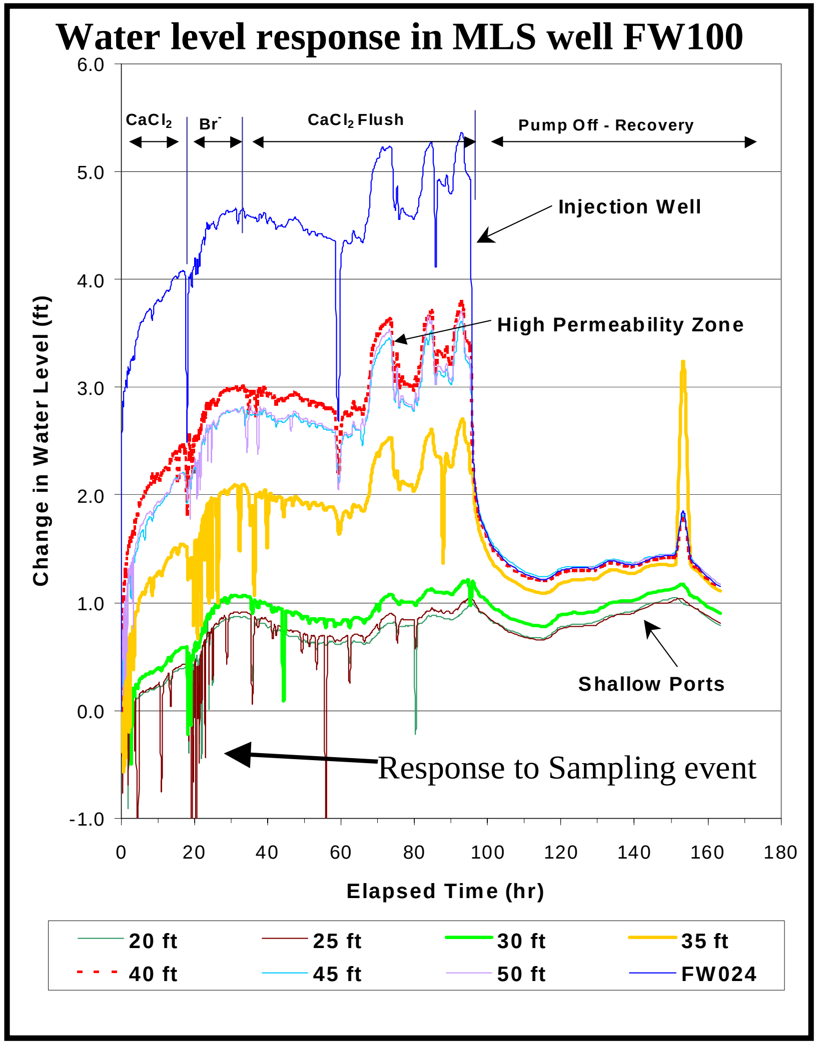


Watson, 2003

Site wide water table monitoring

- Baseline and storm events
- Intensive monitoring during manipultions





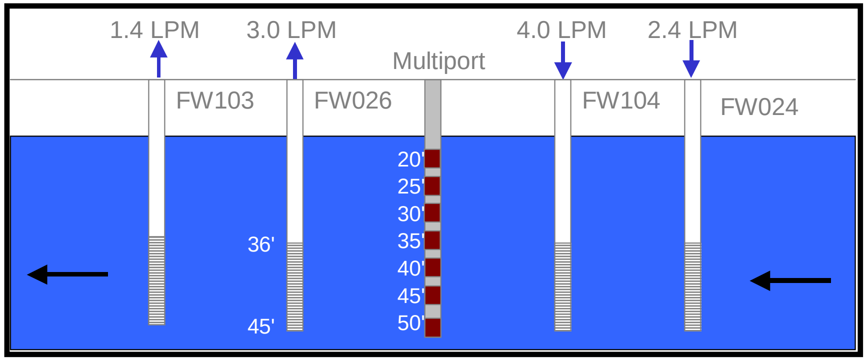
Mehlhorn and Watson, 2003

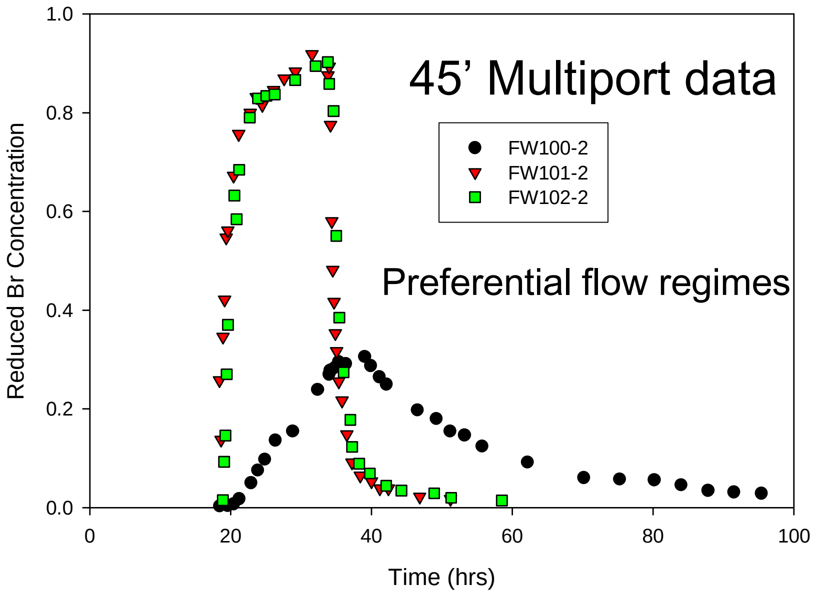
Forced gradient field-scale tracer investigations

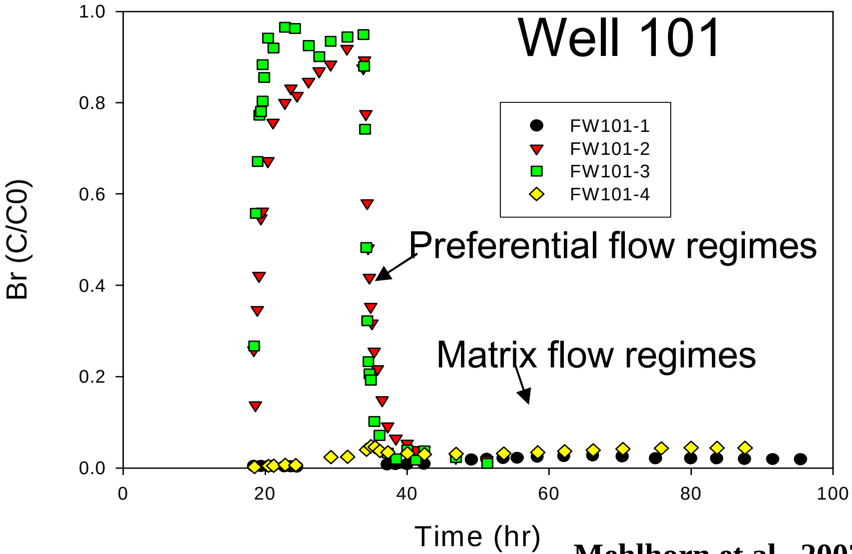
A dual dipole tracer injection-withdraw test was conducted using $CaBr_2$ and $CaCl_2$ in an effort to create an inner and outer hydraulic cage.

Results confirmed location and transport features of preferential flow regimes and slow flowing matrix regimes.

Experimental data was numerically simulated and the model used to design the pending *in situ* U bioreduction system.



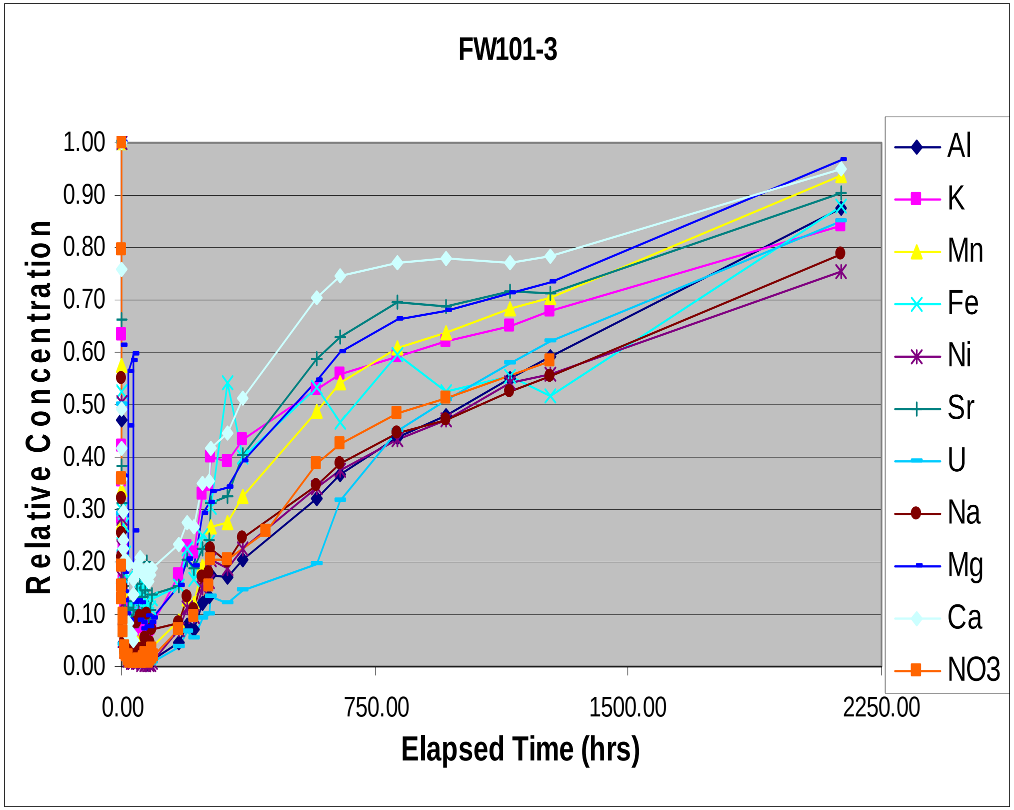


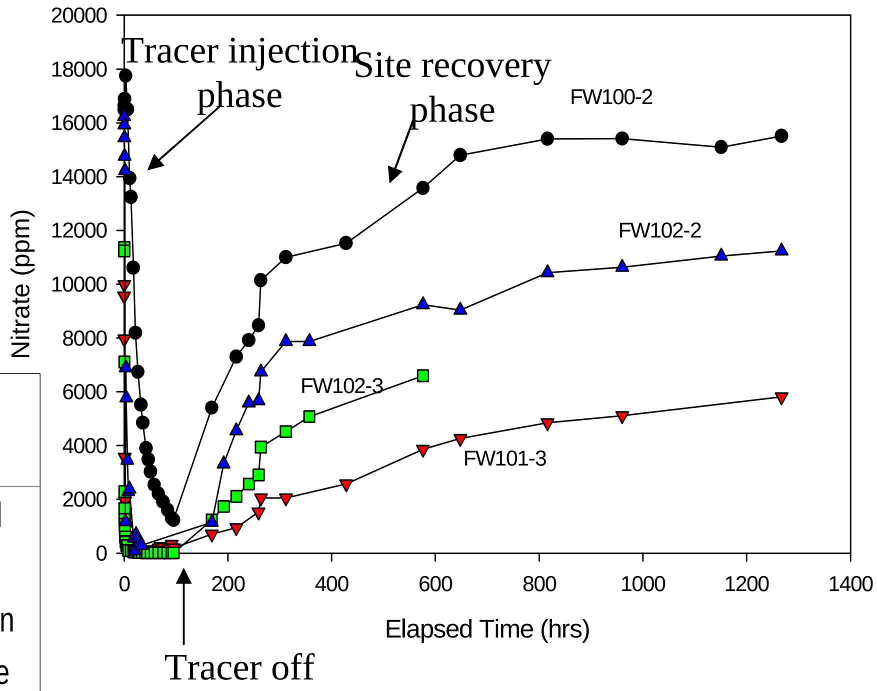


Mehlhorn et al., 2003

Natural gradient site recovery solute breakthrough

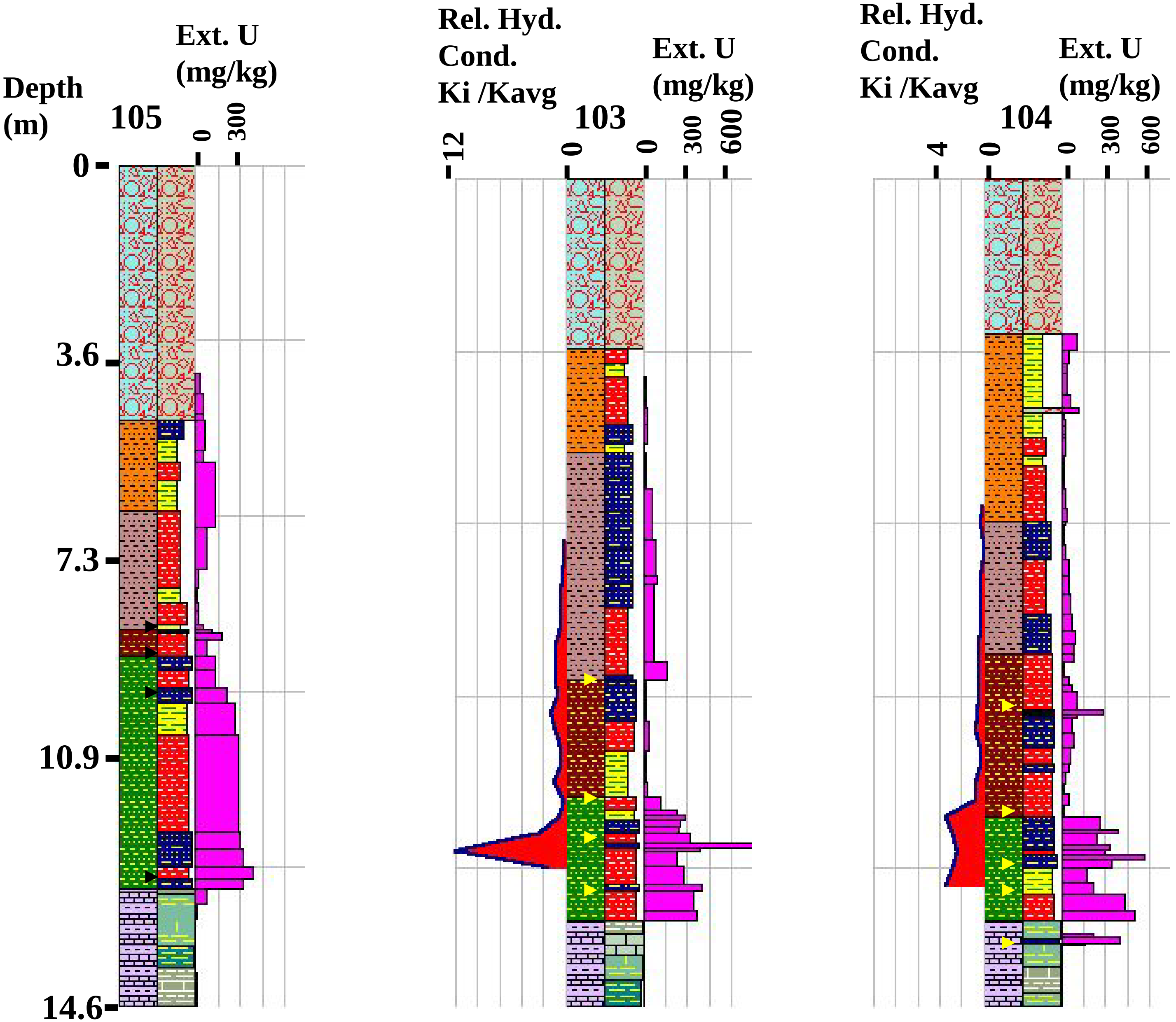
Natural gradient contaminant transport monitored during site recovery. Quantification of solute residence times, direction of groundwater flow, and strike vs. dip interactions.





Mehlhorn et al., 2003

Distribution of Extractable U and Relative Hydraulic Conductivity in the Cores

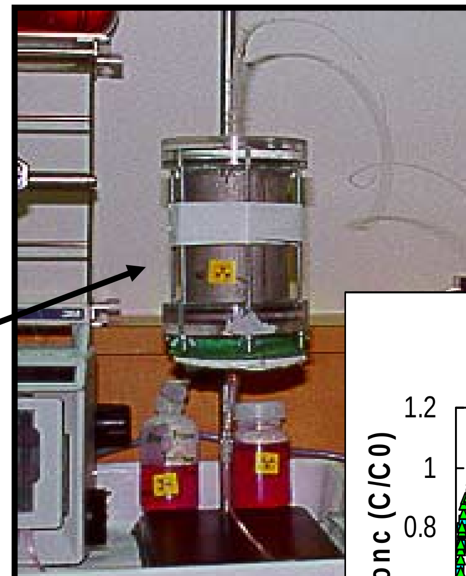


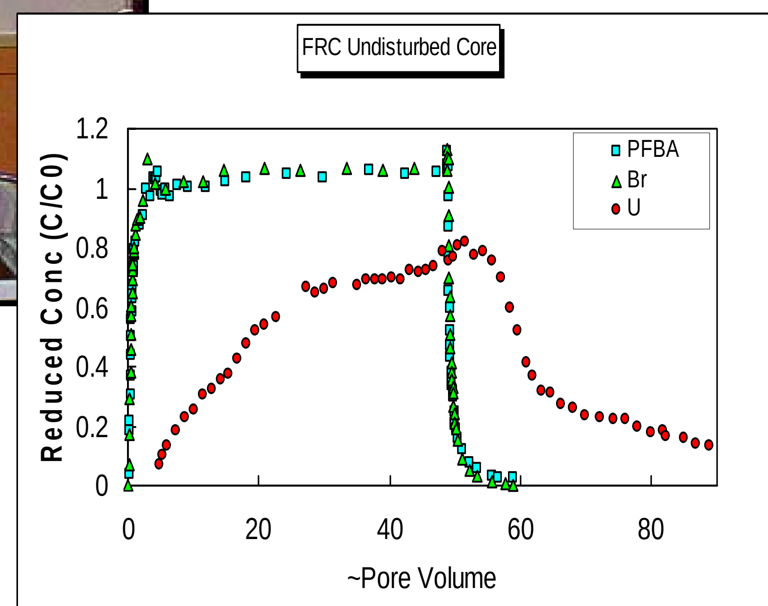
▶ Increases of U at discontinuities

Phillips et al., 2003

Undisturbed column from treatment zone (42 ft. depth)

Laboratory experiments help to quantify solute mass transfer kinetics, uranium reactivity, and propensity for bioreduction under dynamic flow conditions.





Mehlhorn et al., 2003

How is the hydrologic and transport data used?

- Data support the field scale modeling endeavor.
- Supply parameters for direct model input or scale-up (e.g. hydraulic conductivity, mass transfer rates, flow and transport anisotropy ratios, preferential flow vs. matrix diffusion).
- Improved conceptual understanding for enhanced numerical coding and simulation.
- Probable link to microbial community structure and dynamics.
- Provides essential information for the interpretation of geophysical measurements and monitoring.

Aqueous Geochemical Characterization

Intensive site wide monitoring of groundwater chemistry

Inorganic Constituents	Concentrations	Organic Constituents	Concentrations
PH	3.5-3.6	BOD5	100 mg/L*
TIC	202-401 mg/L	COD	200 mg/L*
Chloride	249-298 mg/L	TOC	65-81 mg/L
Sulfate	843-1116 mg/L	2-Butanone	69-84 µg/L
Nitrate	7500-8963 mg/L	Acetone	340-700 µg/L
Nitrite	low	Chloroform	34-36 µg/L
N_2O	???	Ethanol	200 µg/L
Uranium	42-51 mg/L	Tetrachloroethene	2100-3300 µg/L
Tc-99	35-40 nCi/L (80-89 dpm/ml)	Trichloroethene	94-130 µg/L
Ni	11.5-14 mg/L	cis-1,2 Dichloroethene	700-740 µg/L
Cd	0.45 mg/L	Vinyl chloride	2 ug/L
Sb	<0.003 mg/L	1,1,2-trichloro-1,2,2-trifluoroethane	1200-1500 µg/L
Ar	<0.005	methylene chloride	39-42 µg/L
Cr	0.17 mg/L		
Pb	0.03 mg/L		
Se.	0.02 mg/L		

* estimated value: a measurement is needed.

	FW024	FW026
Al	541±47	492±62
Ba	0±0	0±0
Be	0±0	0±0
Ca	931±74	1008±175
Cd	0±0	0±0
Co	1±0	1±0
Cu	1	1±0
Fe	2±0	10±4
K	94±6	93±8
Li	3±0	3±0
Mg	174±11	165±22
Mn	130±9	123±15
Na	859±86	765±91
Ni	12±1	11±1
S	325±30	309±31
Si	28±2	23±3
Sr	2±0	2±0
Zn	2±0	2±1

Al: Precipitate as pH raised.

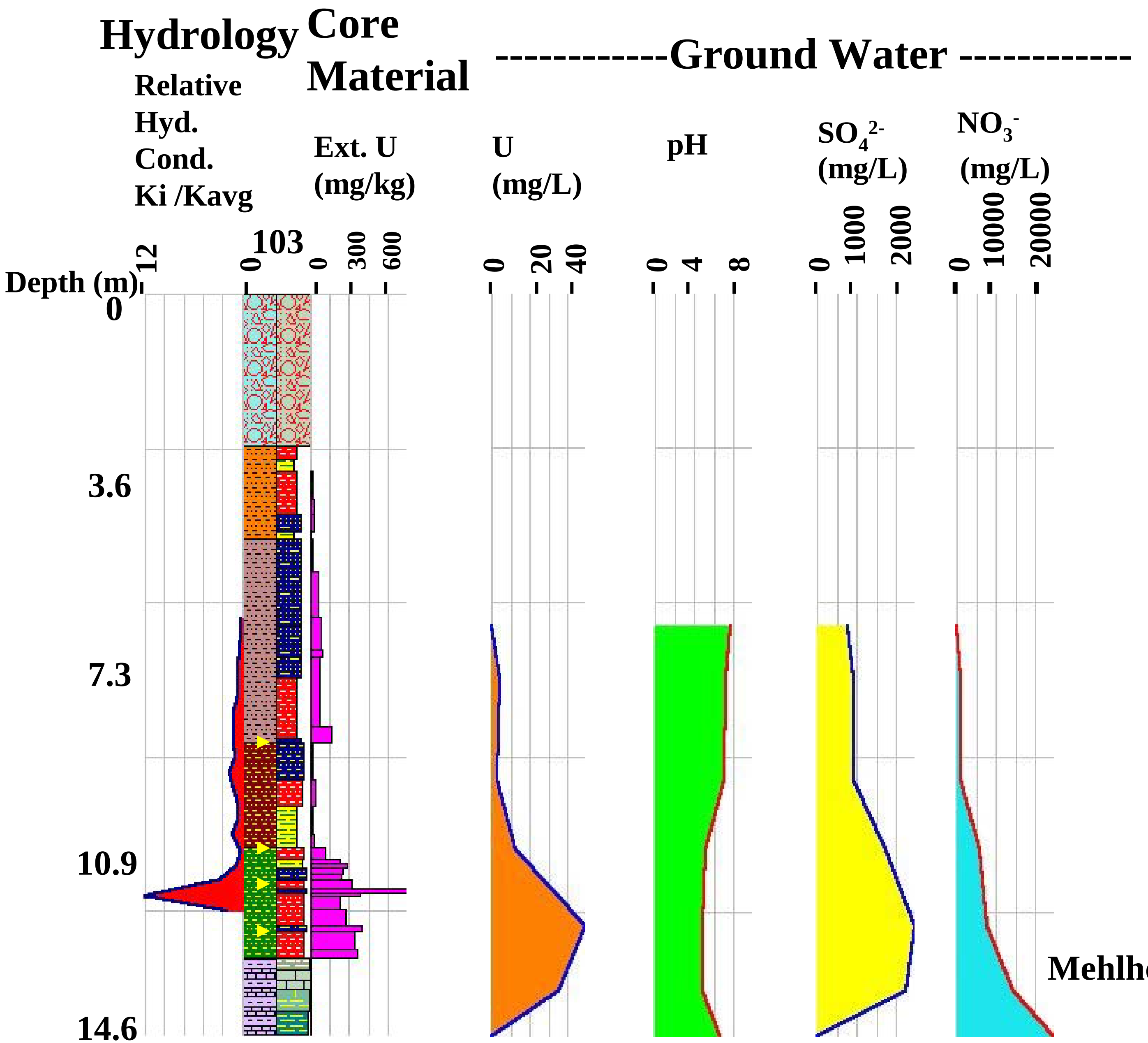
Ca: Precipitate as pH raised.

Mg: Precipitate as pH is raised.

Ni: Toxicity? Eliminated as pH is raised.

Multiple investigators

Coupled groundwater chemistry with solid phase constituents and hydrology



Mehlhorn and Phillips, 2003

Molecular speciation using X-ray Absorption Spectroscopy

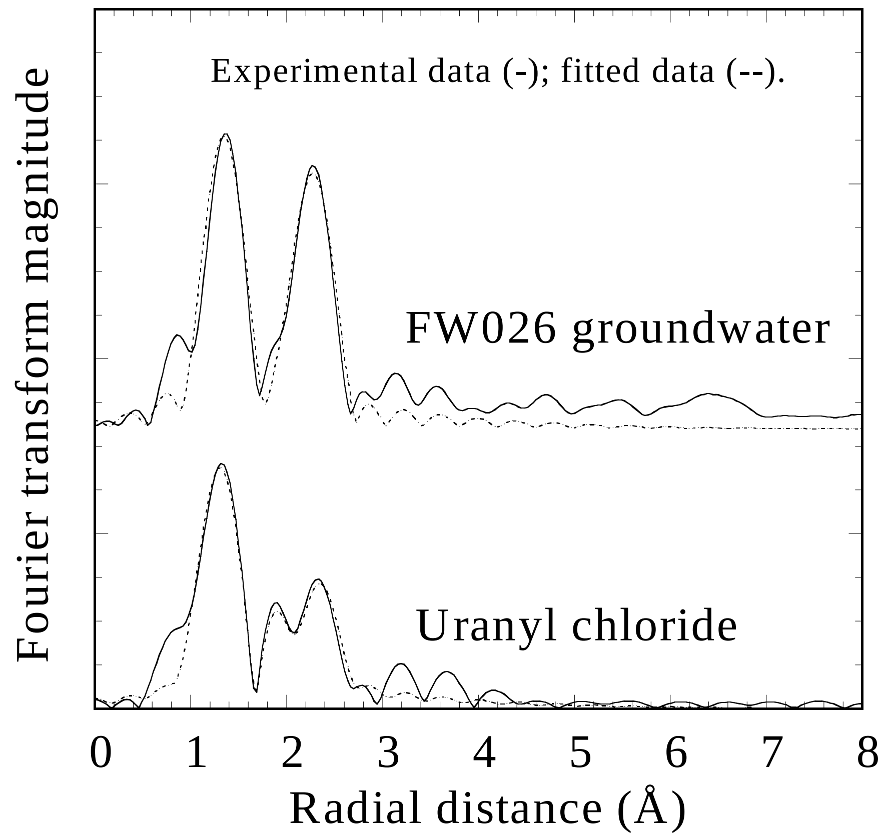


Figure 2. EXAFS analysis of freeze-dried FRC groundwater sample FW026 indicated uranium is present as uranyl chloride.

Francis et al., 2003

Field-portable Immunosensor

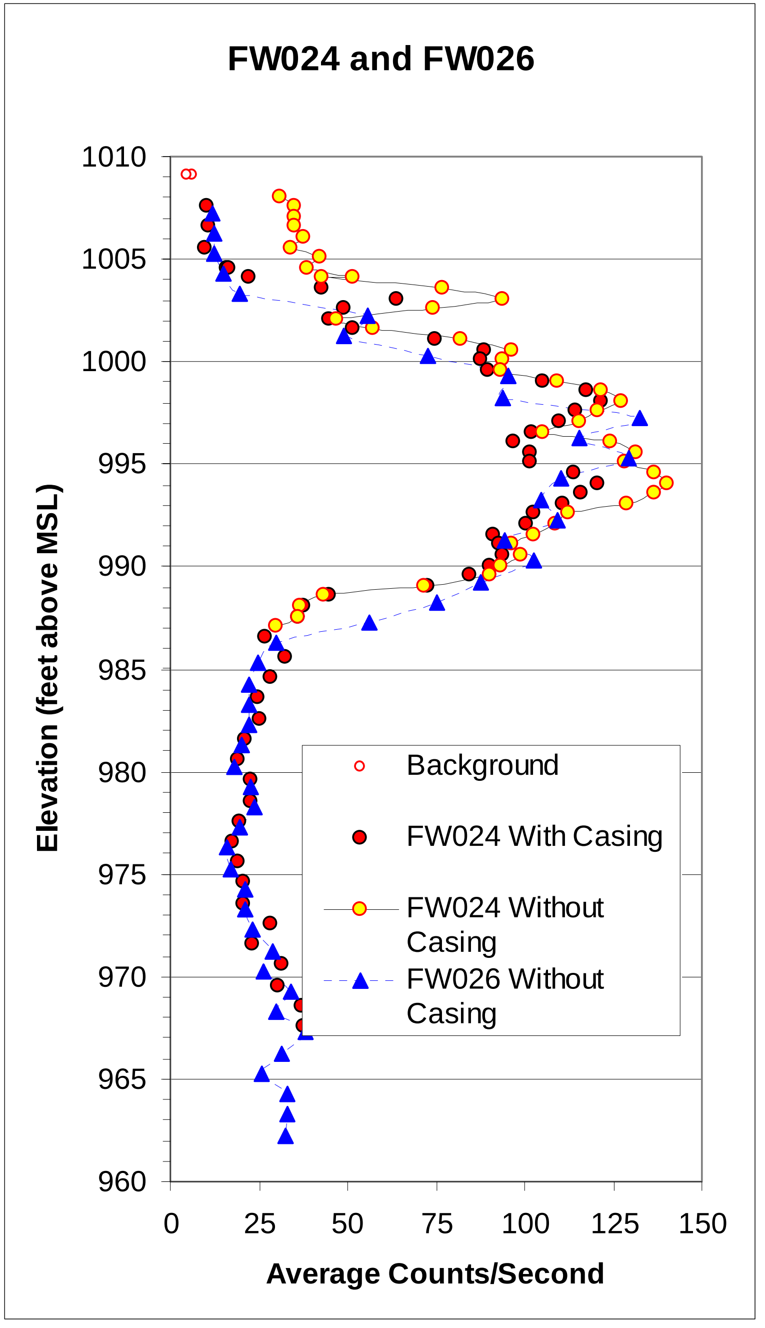
Field-portable Immunosensor for real-time analysis of U(VI) in groundwater.

How is the aqueous geochemical data used?

- Data support the lab and field scale modeling endeavors.
- Supply parameters for direct model input (e.g. solute speciation, mass balance, spatial and temporal concentration distributions).
- Improved conceptual understanding for enhanced numerical coding and simulation.
- Important link to microbial community structure and dynamics.
- Provides essential information for the interpretation of solid phase geochemistry and mineralogy.

Solid Phase Geochemical and Mineralogical Characterization

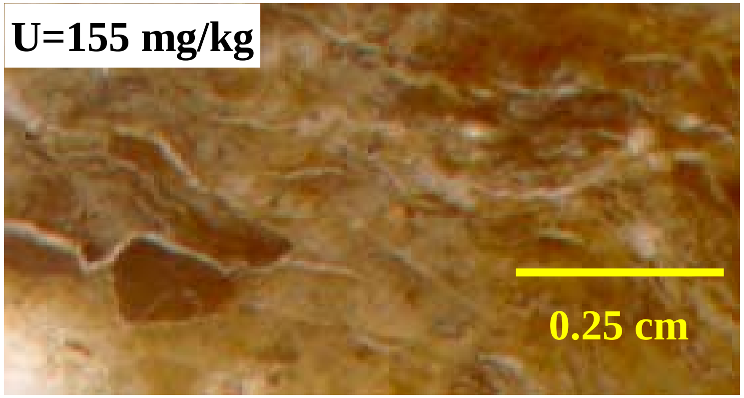
Natural gamma-ray logs showing ^{232}Th and U isotope accumulations in clay rich zones vs. shale saprolite dominated zones.



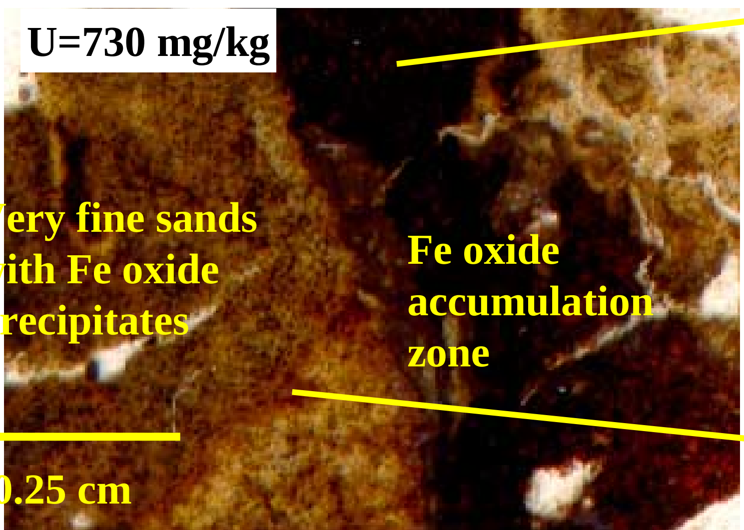
Watson, 2003

Area 3 Core Mineralogical Evaluations

Overlying Gleyed leached flow zone with high U, low pH groundwater



Black precipitate Zone with higher pH and lower U in groundwater

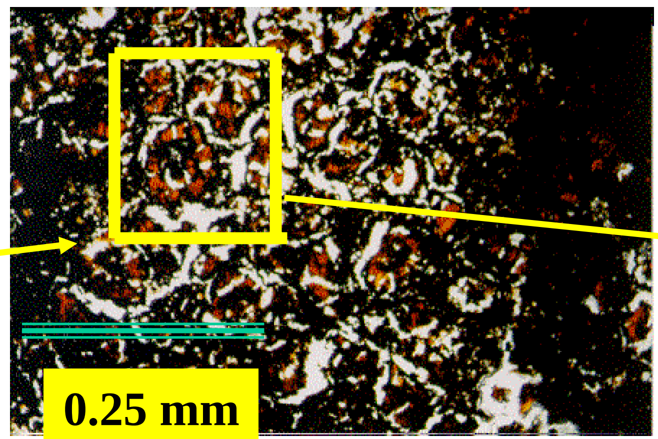


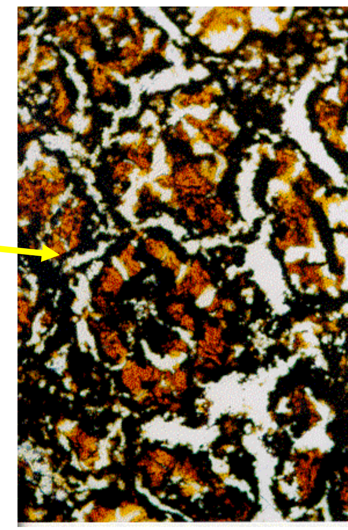
A high U zone was detected in FW100 (Area 3 field site) at a depth of 46'.

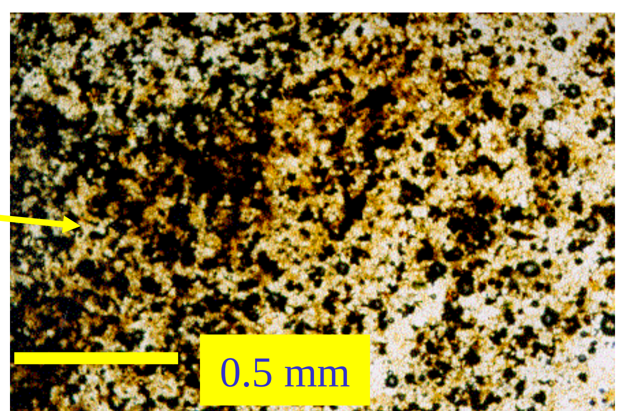
XRD results:

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

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



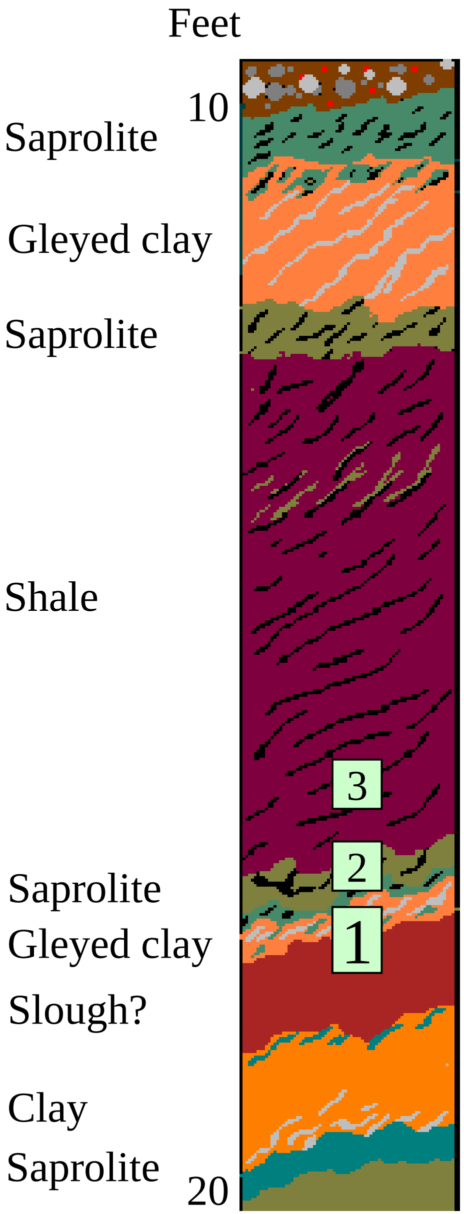




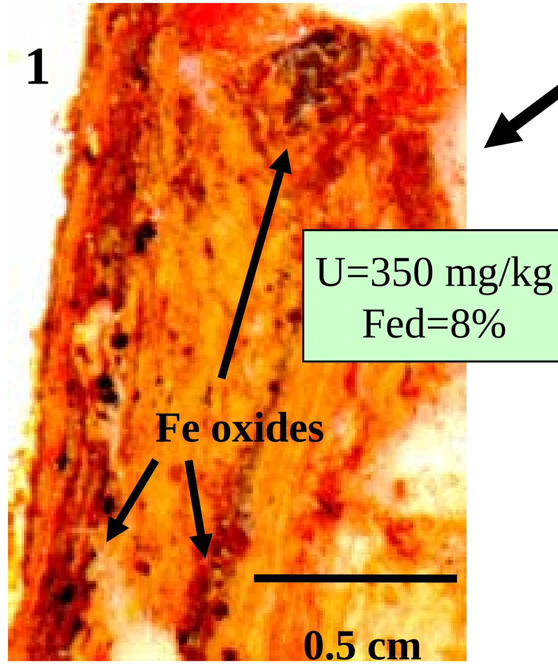
Roh and Watson, 2003

Area 1 Core Analysis

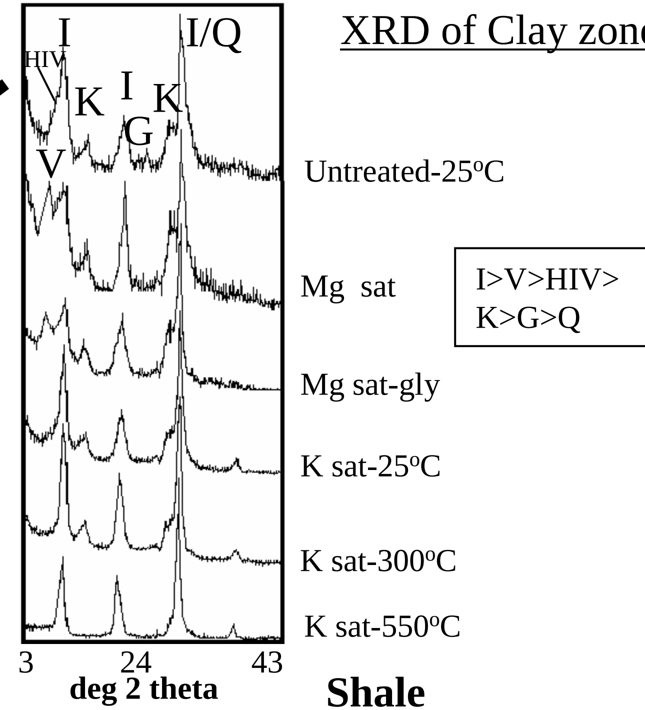
Core 21



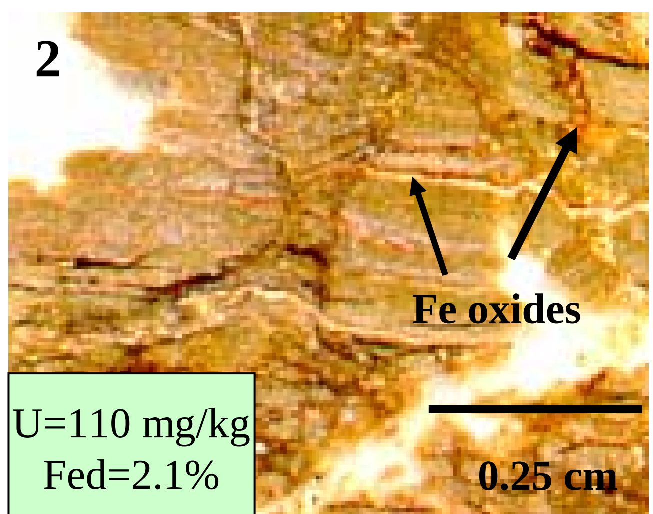
Fe rich clay zone



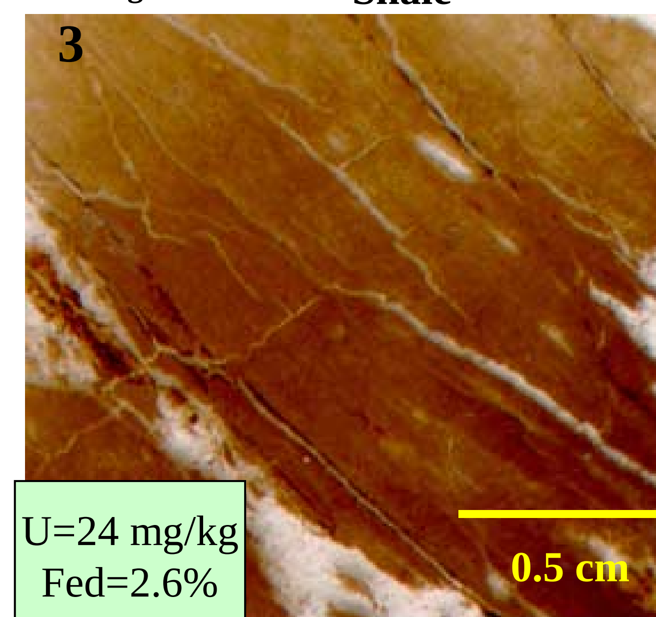
Roh and Watson, 2003



Highly weathered leached saprolite

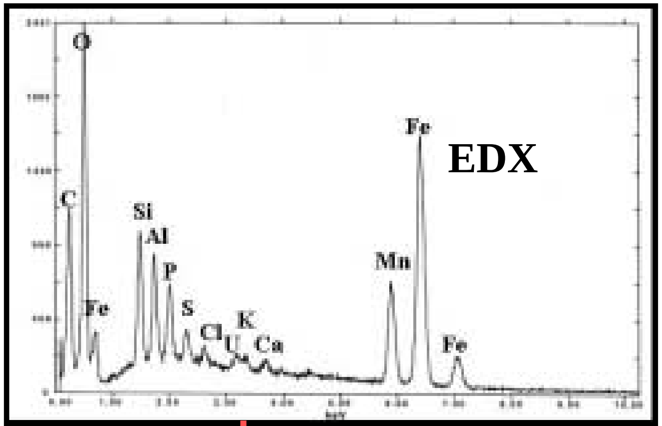


Shale

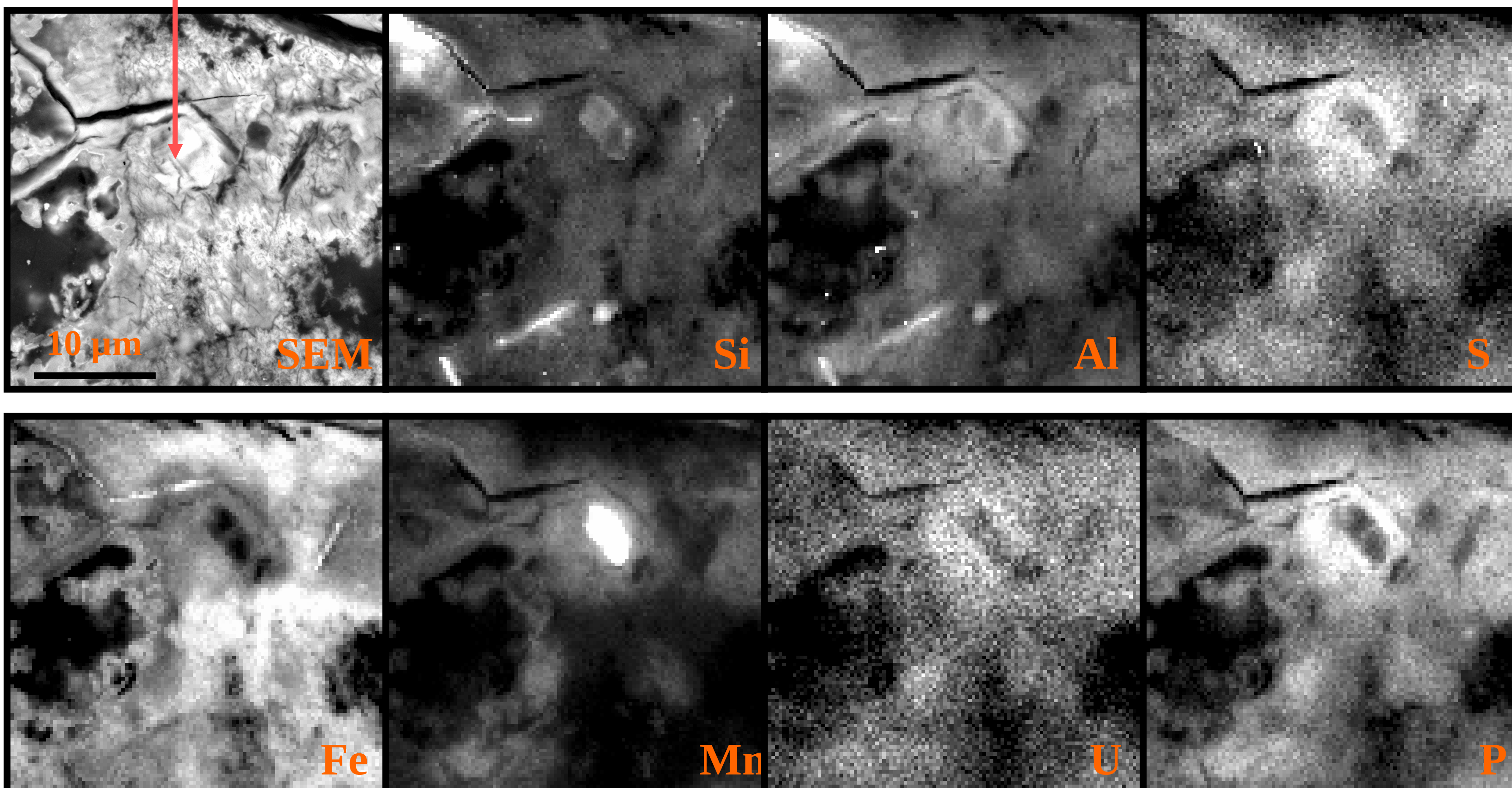


Roh and Watson, 2003

SEM-BSE-Element Mapping of FWB100-06-09 sample Black Rad Zone

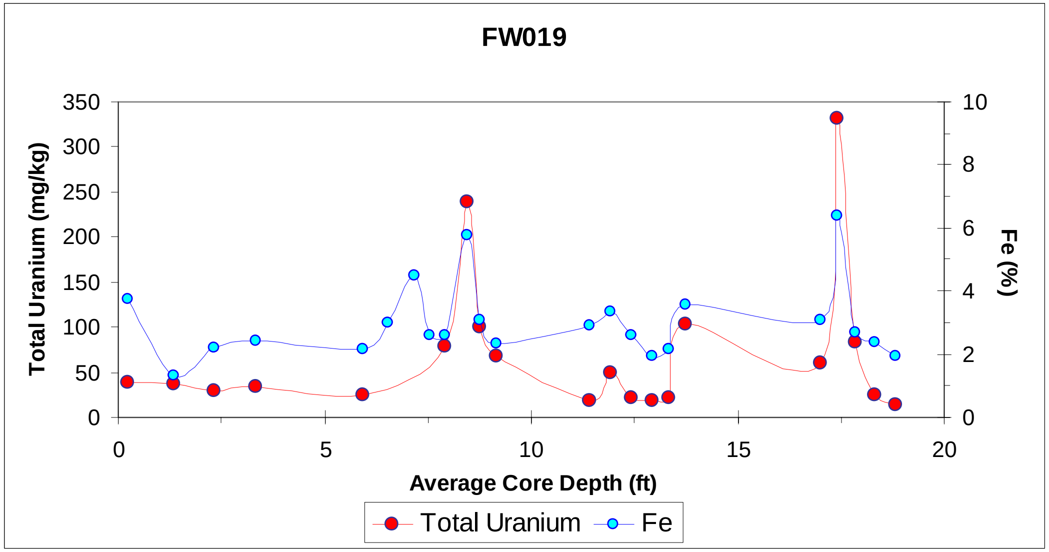


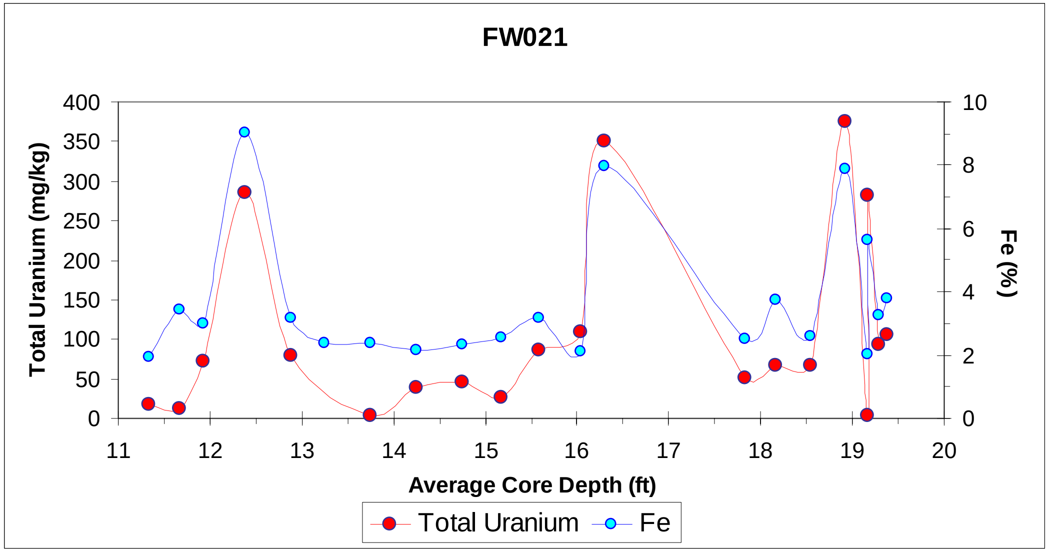
U distribution matches P and S distribution



Comparison of U versus Fe concentrations in sediments at the OSU / OU Site

Excellent correlation observed at FW019 and FW021



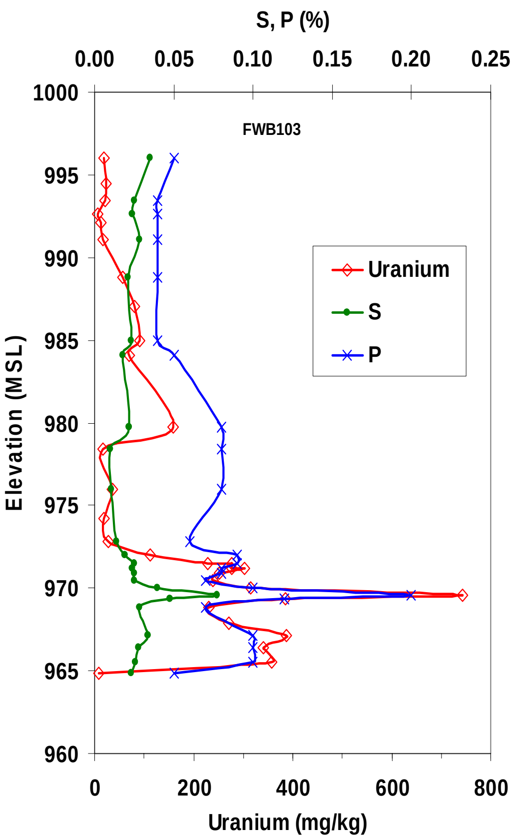


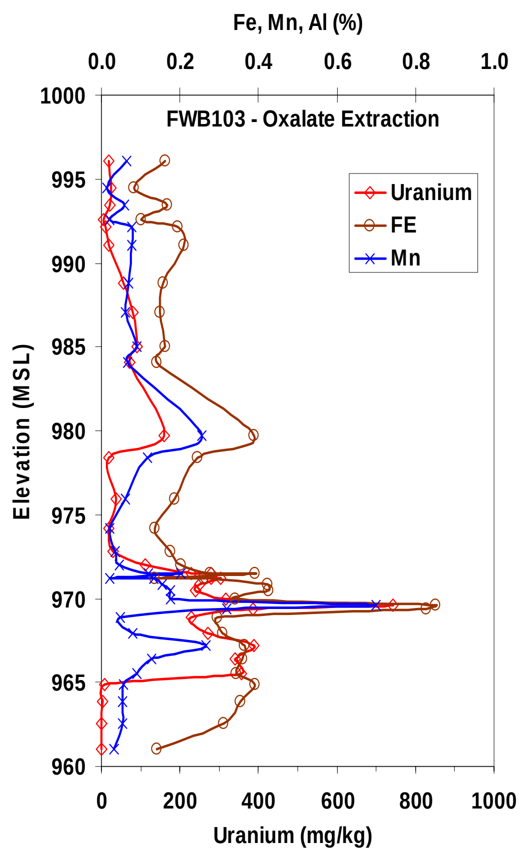
Watson et al., 2003

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

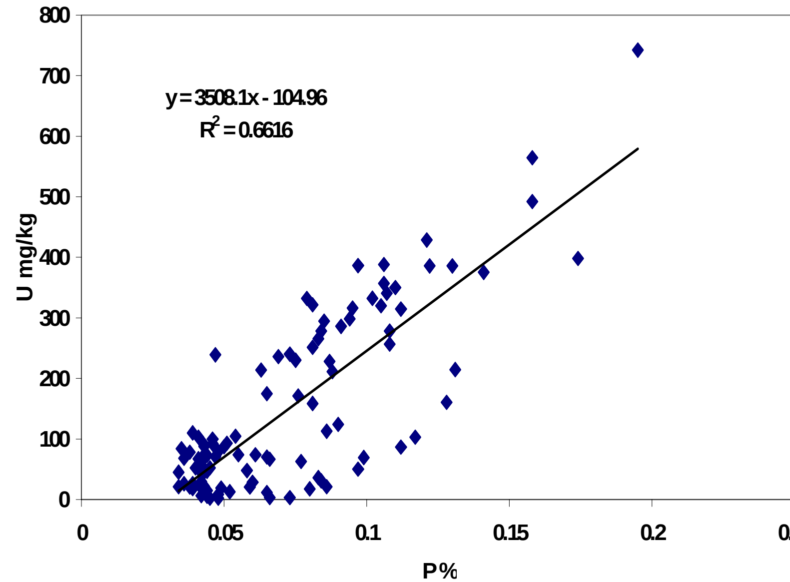
- Correlation varies form core to core and between depth intervals
- P is as high as 0.2 %
- P and S are correlated to U

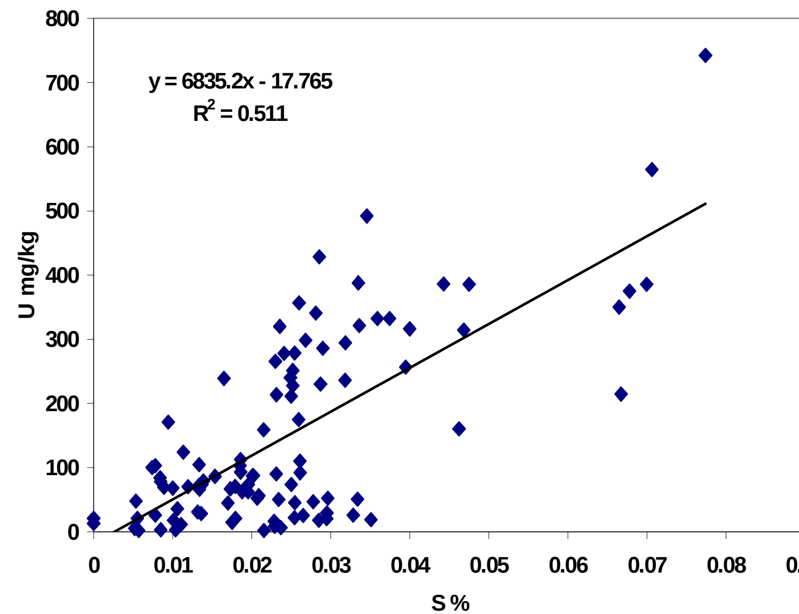
FW103 distribution with depth
- Strong association with U





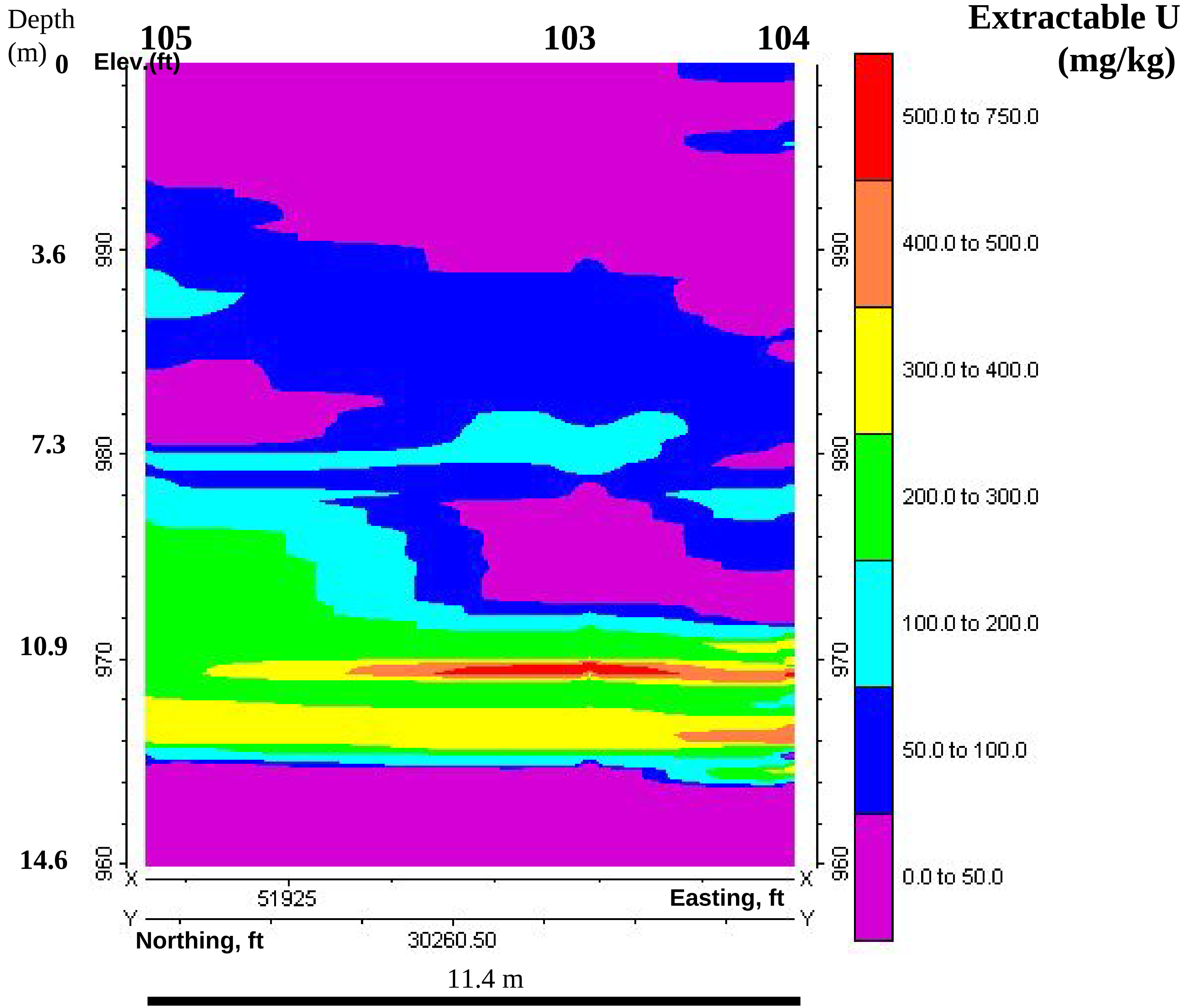
Area 3 and Area 1 samples





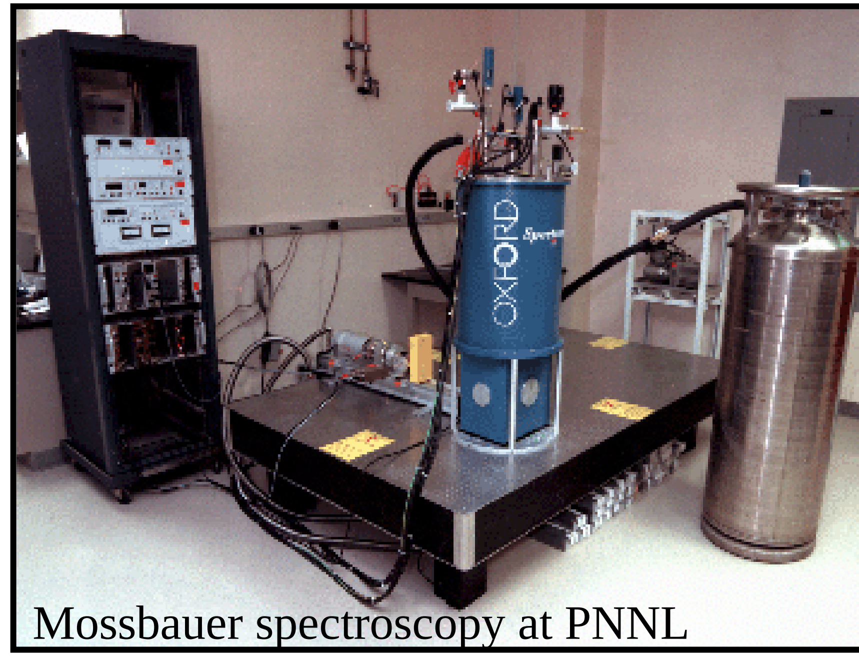
Watson et al., 2003

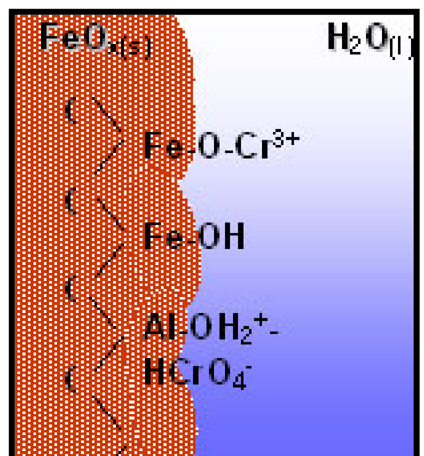
Interpolated Uranium Distribution between the Cores

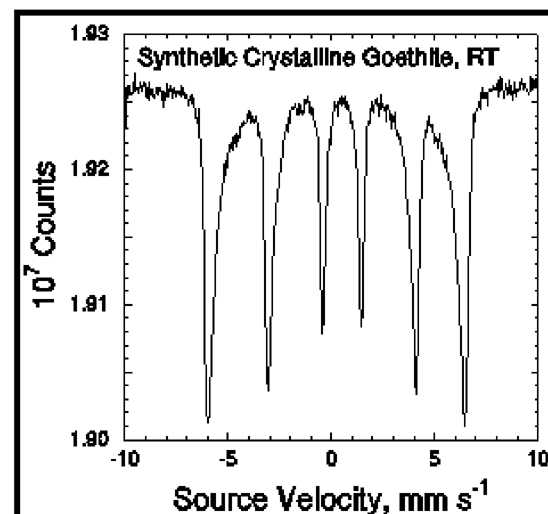


Mossbauer used to quanfity the types and amount of various Fe-bearing oxides in heterogeneous FRC background and contaminanted samples (Area 1).

Also use quantify changes in Fe mineralogy following in situ biostimulation using various electron donors (Background and Area 1).


Mossbauer spectroscopy at PNNL

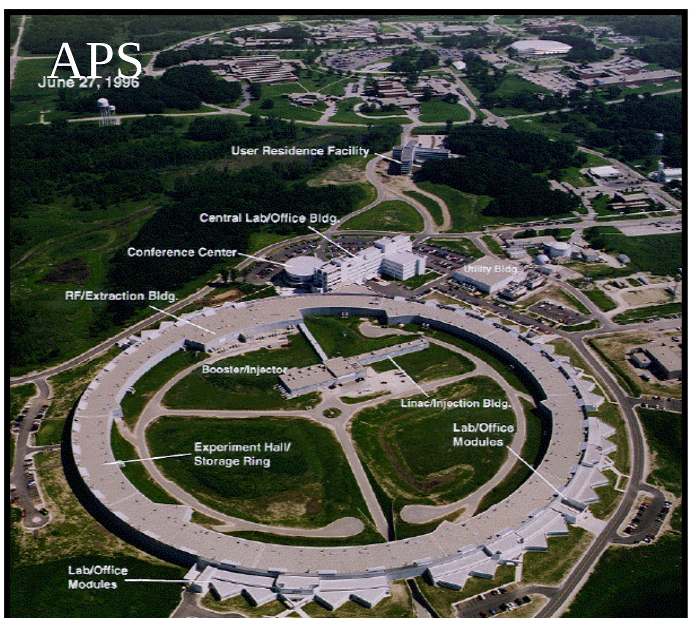


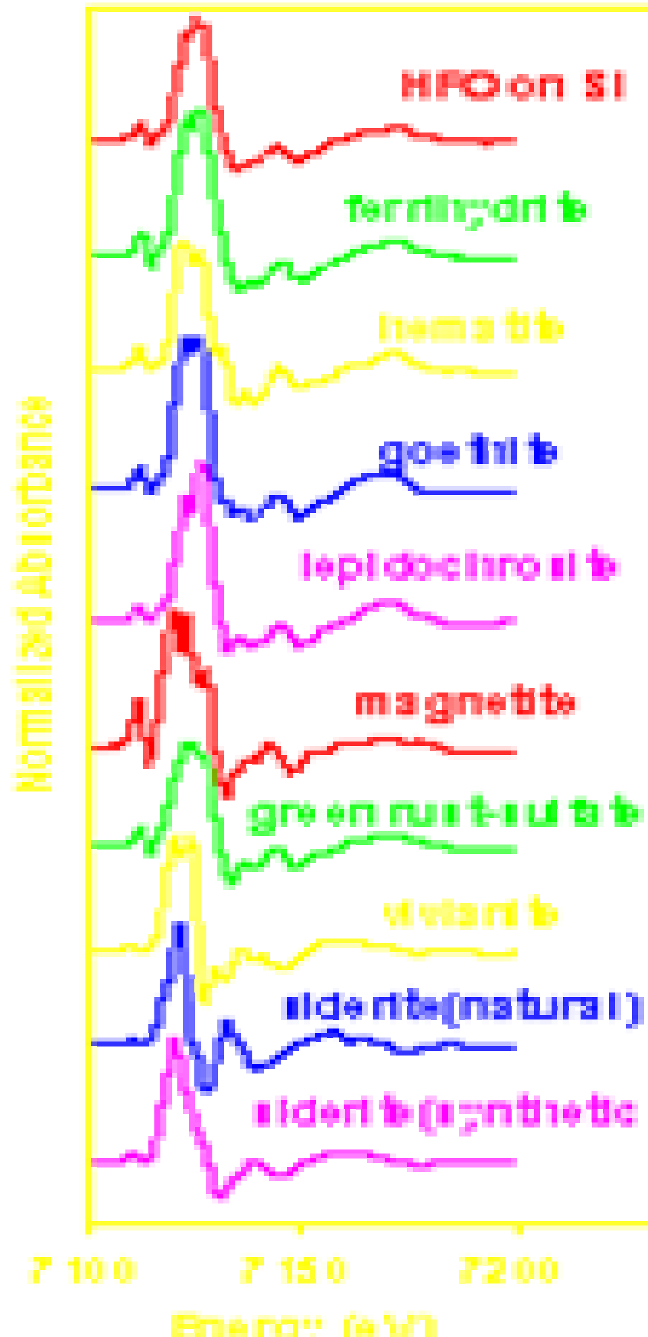


Stucki et al., and Zachara et al., 2003

Extended X-ray Absorption Fine Structure (EXAFS) used to quantify the Fe-oxide mineralogy in heterogeneous samples from the FRC (Area 3).

Fendorf, 2003





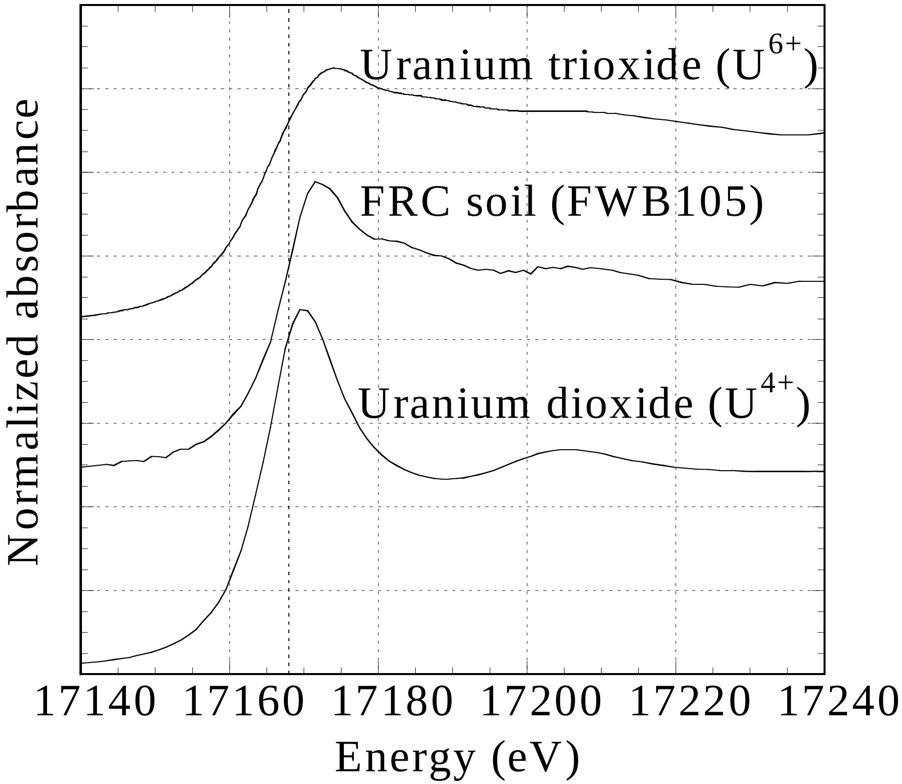


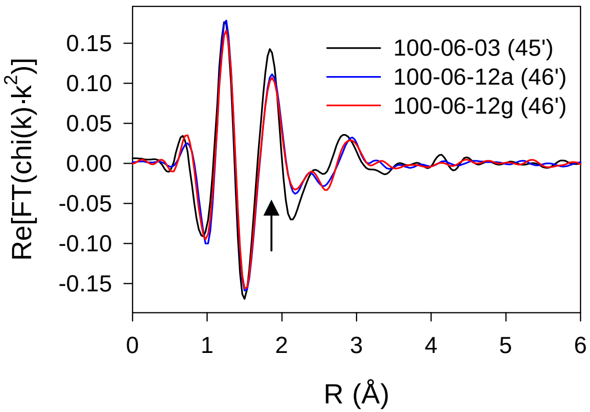
Figure 1. XANES analysis of FRC soil sample shows uranium is in hexavalent form.

Francis, 2003

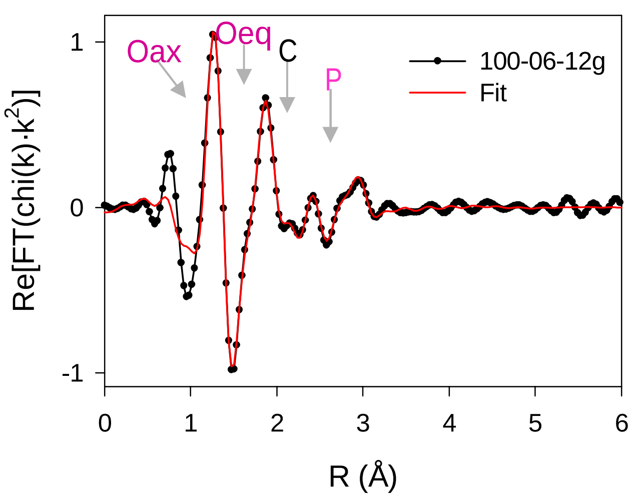
XANES used to quantify valance state of sorbed U (e.g. U(IV) vs. U(VI)).

U L_3-edge XAFS data collected from Field Research Center soil samples

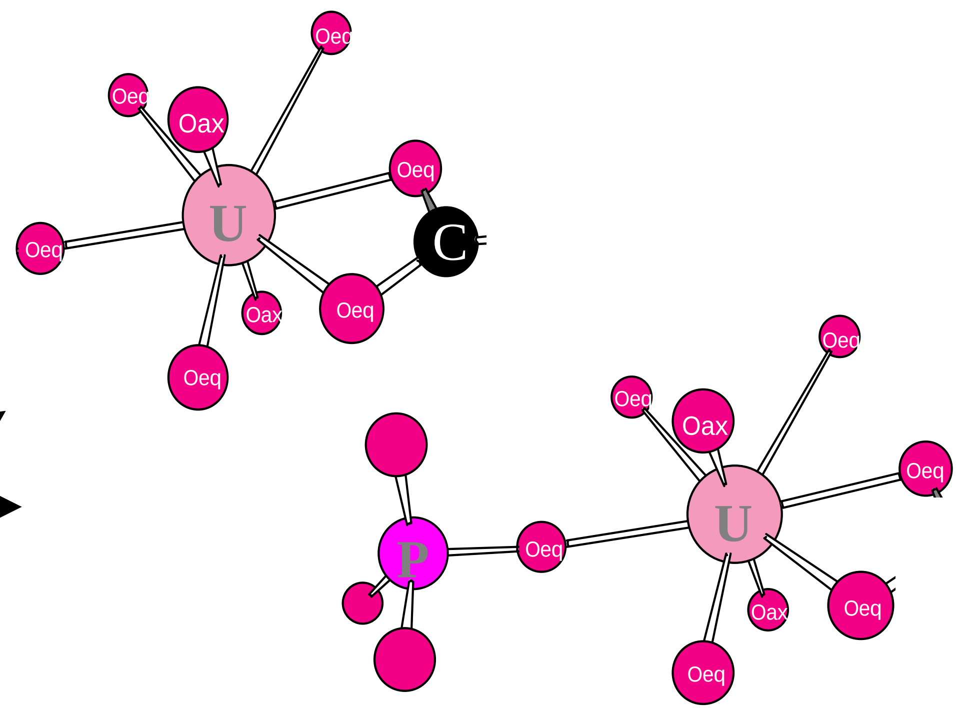
Real part of Fourier transform of data from samples taken at 45, and 46 (with replicate) feet



Real part of Fourier transform of data and model from sample taken at 46 feet



- XAFS used to quantify the chemical environment of solid phase U at the FRC.
- Model of the data at 46 feet show that U is coordinated by bidentate carbon containing groups and/or monodentate phosporous containing groups.

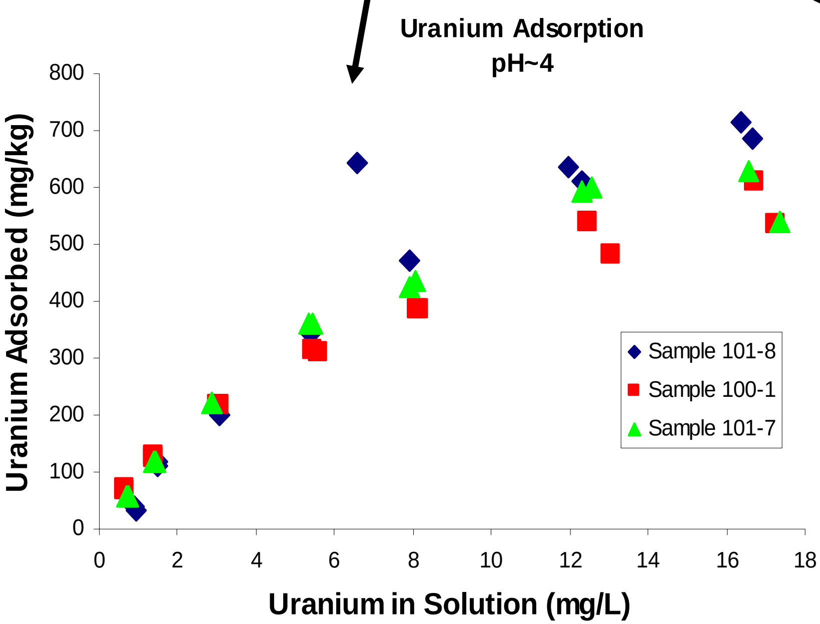


Kelly and Kemner, 2003

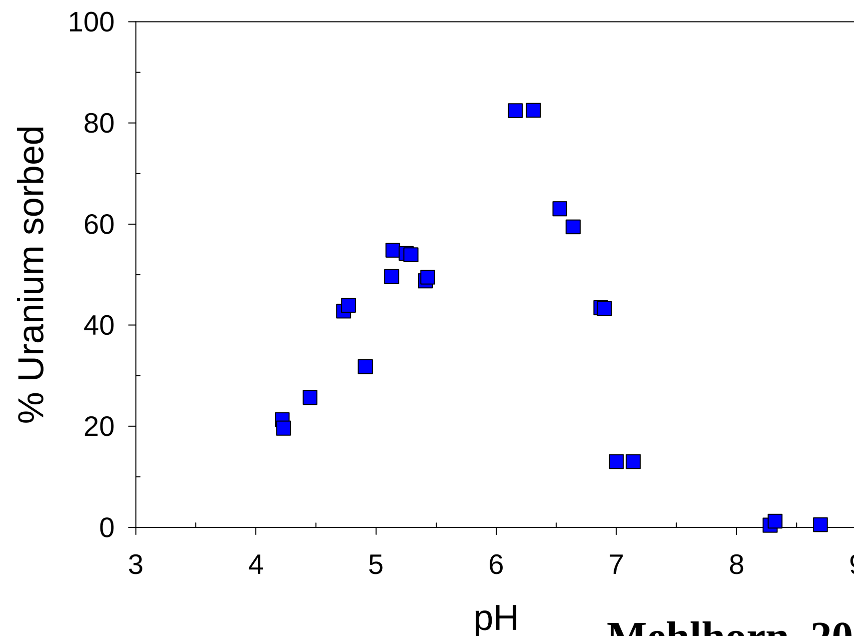
Macroscopic uranium adsorption on FRC soils

Concentration dependent U sorption on FRC soils.

U sorption is strongly pH dependent.



Uranium Sorption Edge with 1% CO_2(g)

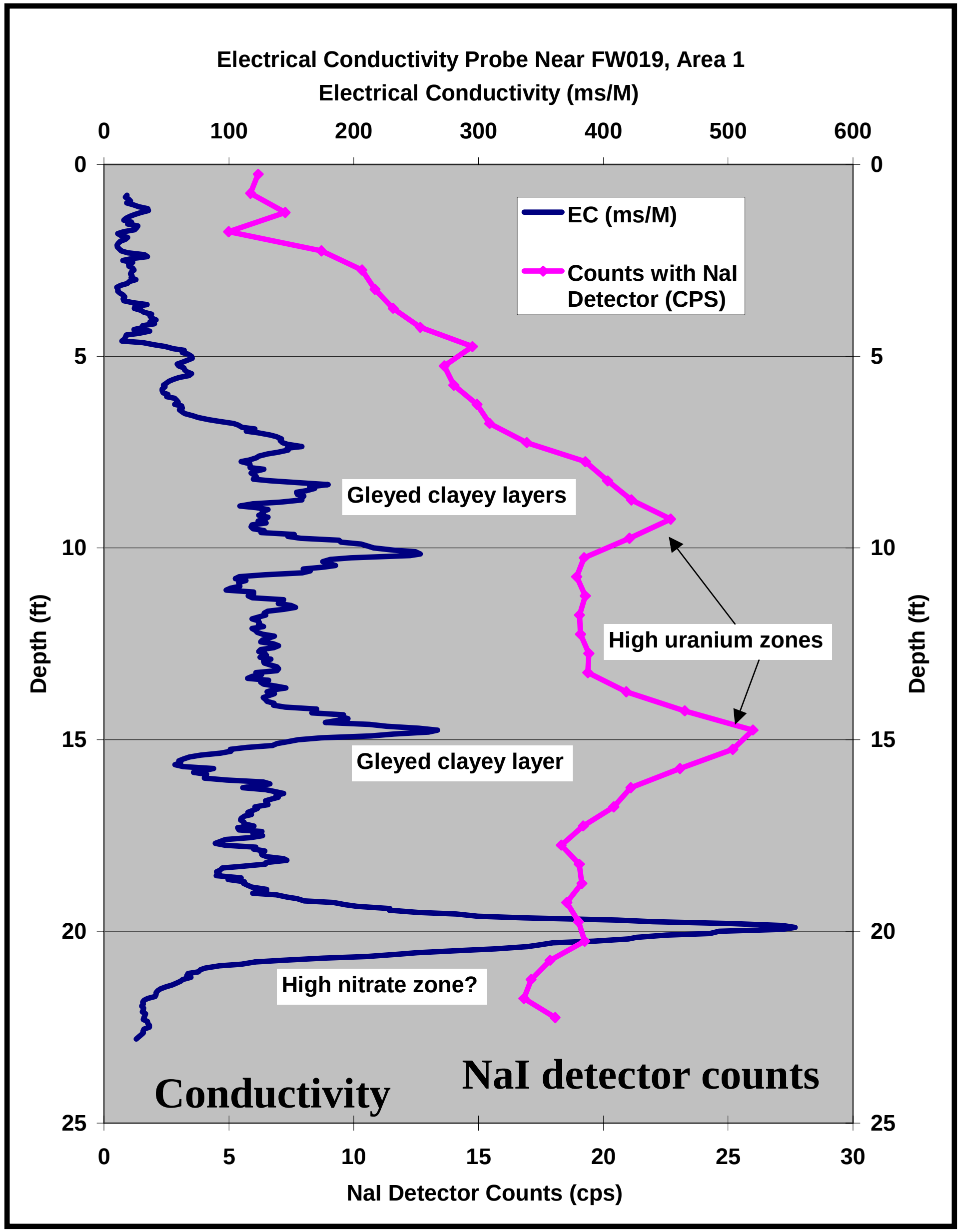


Mehlhorn, 2003

How is the solid phase geochemical and mineralogical data used?

- Mineralogy confirm whether hypothesized reaction pathways and associated stability/equilibrium constants are correct.
- Solid phase contaminant speciation used to understanding in situ geochemical and microbial processes.
- Supply parameters for direct model input (e.g. solute speciation, mass balance, spatial and temporal concentration distributions).
- Improved conceptual understanding for enhanced numerical coding and simulation.
- Important link to microbial community structure and dynamics.
- Provides essential information for the interpretation of geophysical measurements and monitoring.

Geophysical Characterization

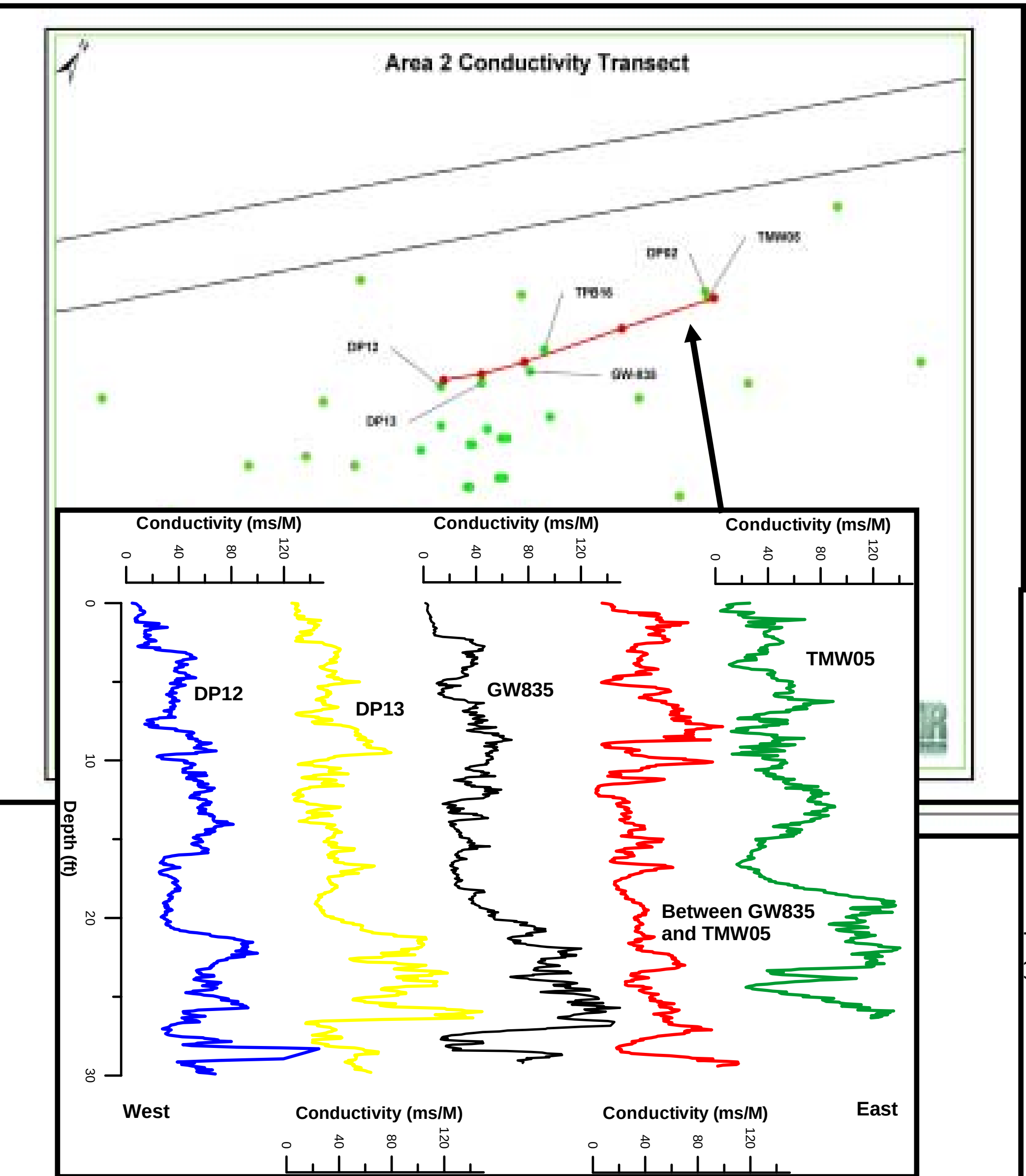


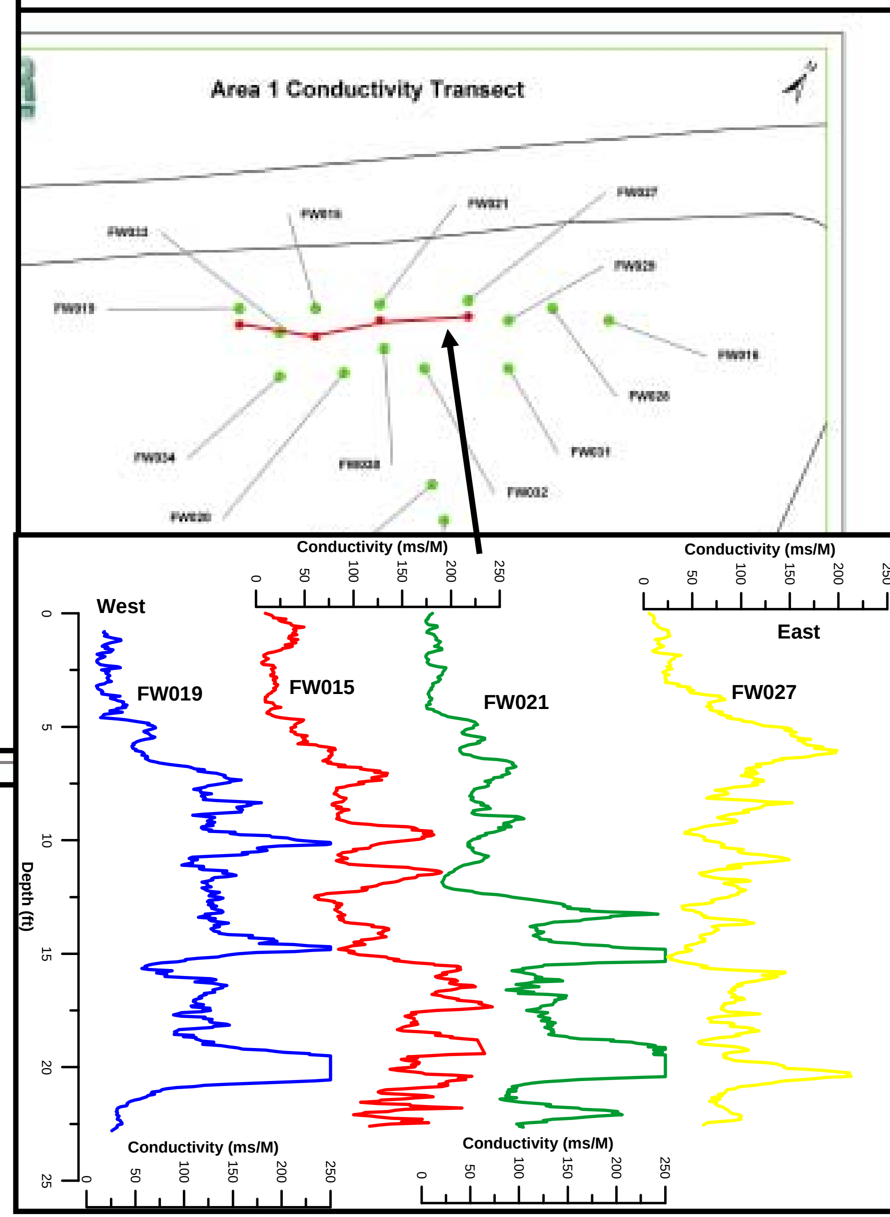
Electrical Conductivity Probing with FRC Geoprobe

- Useful for mapping stratigraphy and high U zones

Watson and Hyder, 2003

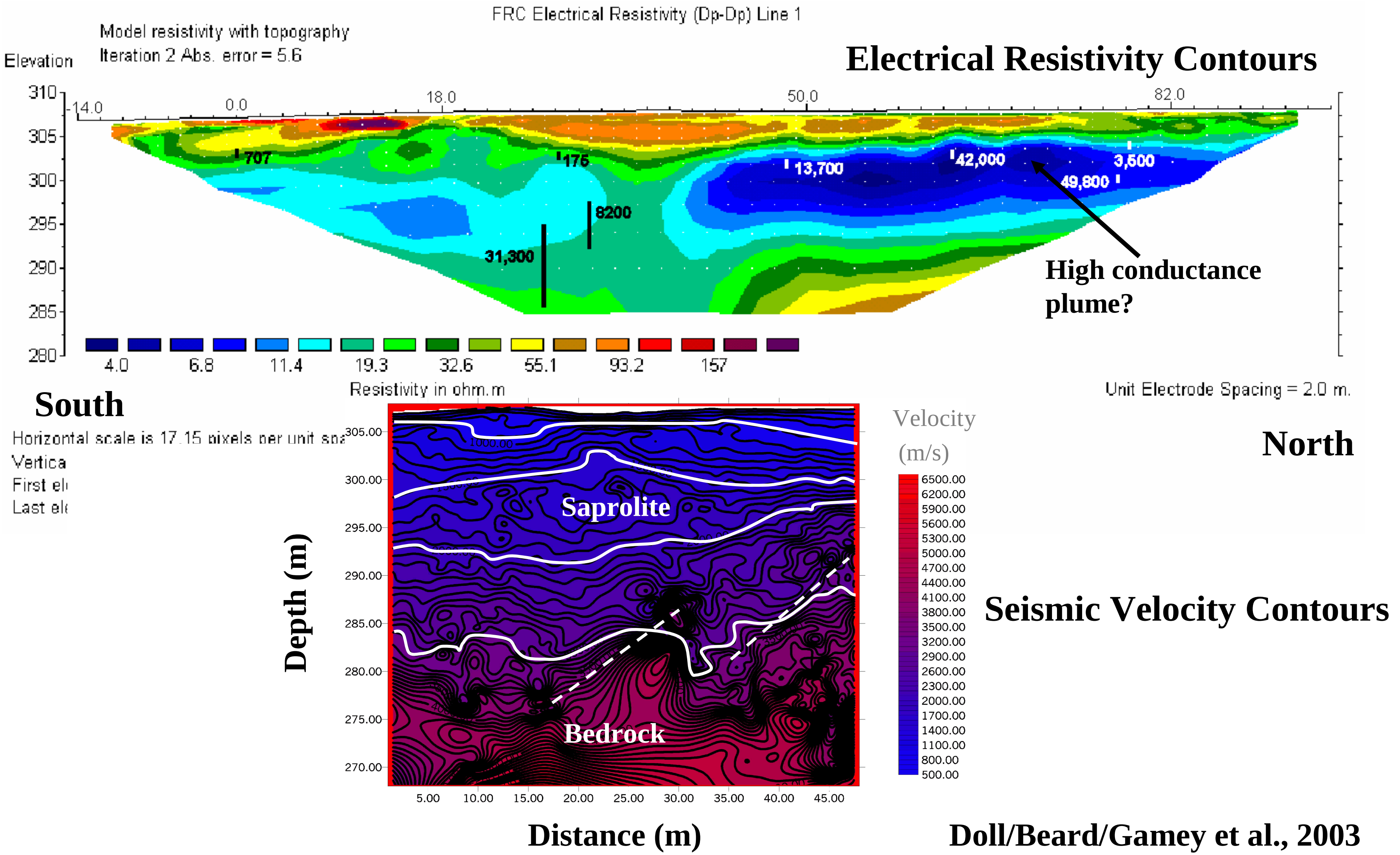
Electrical conductivity Profiling





Watson and Hyder, 2003

Seismic and Resistivity Surveys

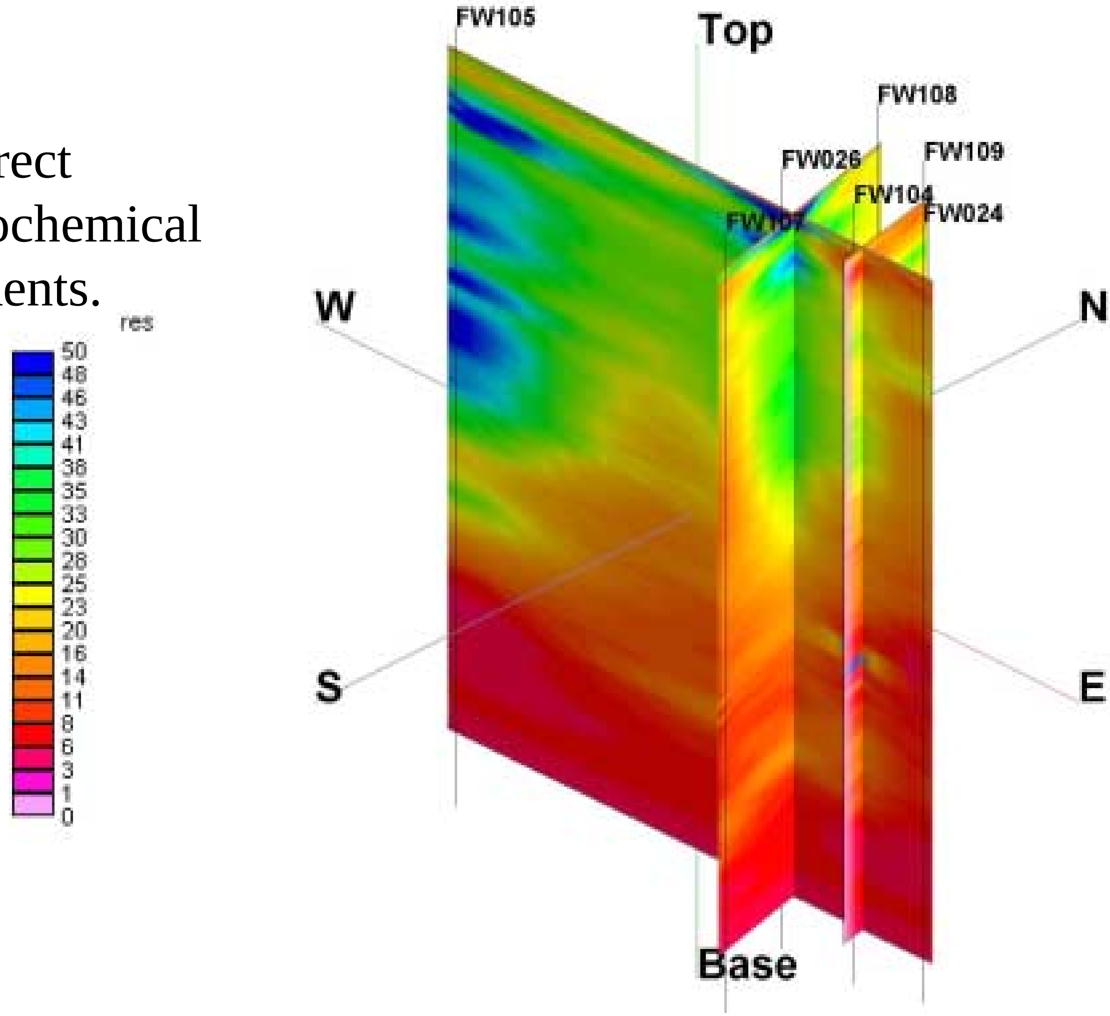


Doll/Beard/Gamey et al., 2003

Electromagnetic Induction Logging

Spatial and temporal plume mapping during manipulation.

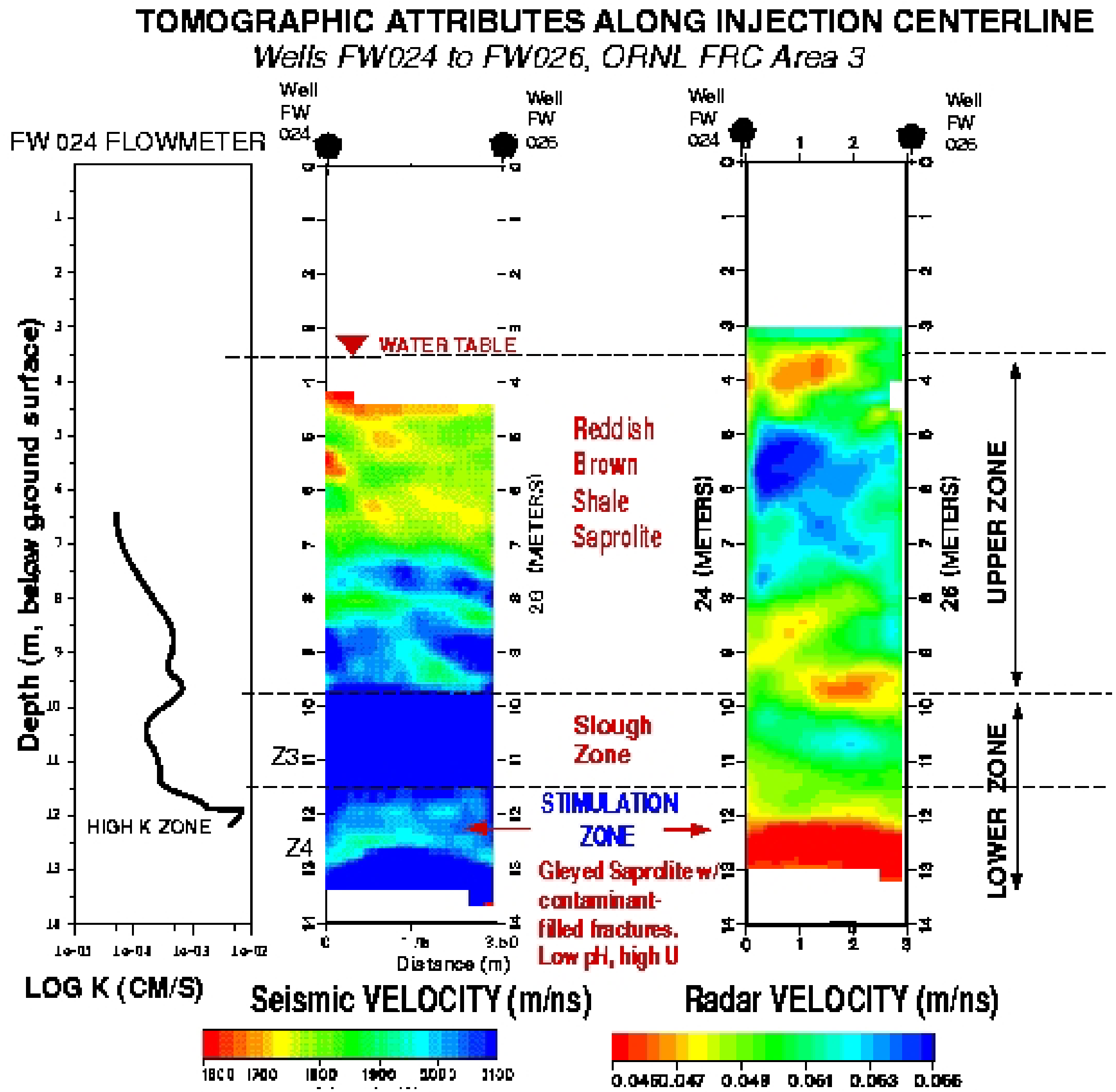
Compliments direct groundwater geochemical tracer measurements.



Doll/Beard/Gamey et al., 2003

Seismic and Radar Tomography

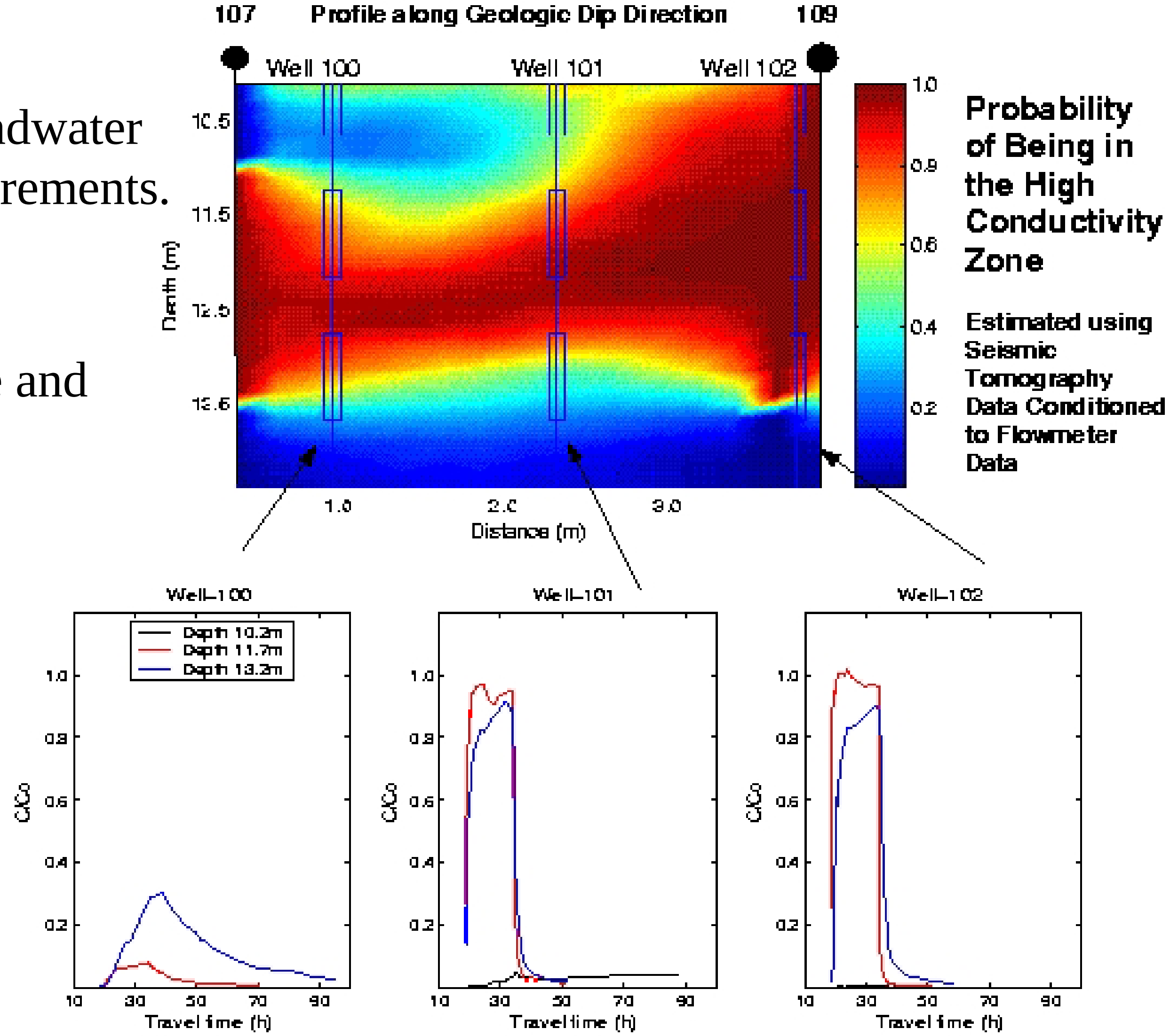
Mapping subsurface material heterogeneities using cross-borehole techniques.



Hubbard et al., 2003

Compliments direct groundwater geochemical tracer measurements.

Provides complementary information on in situ fate and transport processes.



Hubbard et al., 2003

Mehlhorn et al., 2003

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

How is the geophysical data used?

- Provides essential information on media structure and large-scale plume identification.
- Provides complementary information on in situ fate and transport processes.
- Provides large-scale view of subsurface features for guiding groundwater well placement.
- Proven and potential applications for monitoring hydrological, geochemical, and microbial manipulations.
- Supply integrated, large-scale subsurface data sets that can be compared to transport model simulations/visualizations.
- Used to estimate hydrogeochemical parameters for use in transport models.
- Improved conceptual understanding for enhanced numerical coding and simulation.

Who is coordinating with who and why?

Criddle/Jardine project

Watson: assistance with groundwater and solid phase geochemical analyses and infrastruture support.
Roh: mineralogy and solid phase elemental mapping.
Kemner: solid phase U speciation using XAFS
Fendorf: solid phase Fe speciation using XAFS
Doll: geophysical plume mapping using surface and subsurface monitoring techniques.
Hubbard/Fienin: geophysical plume mapping and model parameter estimations using cross-hole.
Blake: groundwater U monitoring in real-time.

Istok/Krumholtz etc. project

Watson:

Stucki/Zachara

Roh

Blake