Studies of diffusion and reaction processes in porous rocks: examples from nuclear waste management and contaminant hydrogeology

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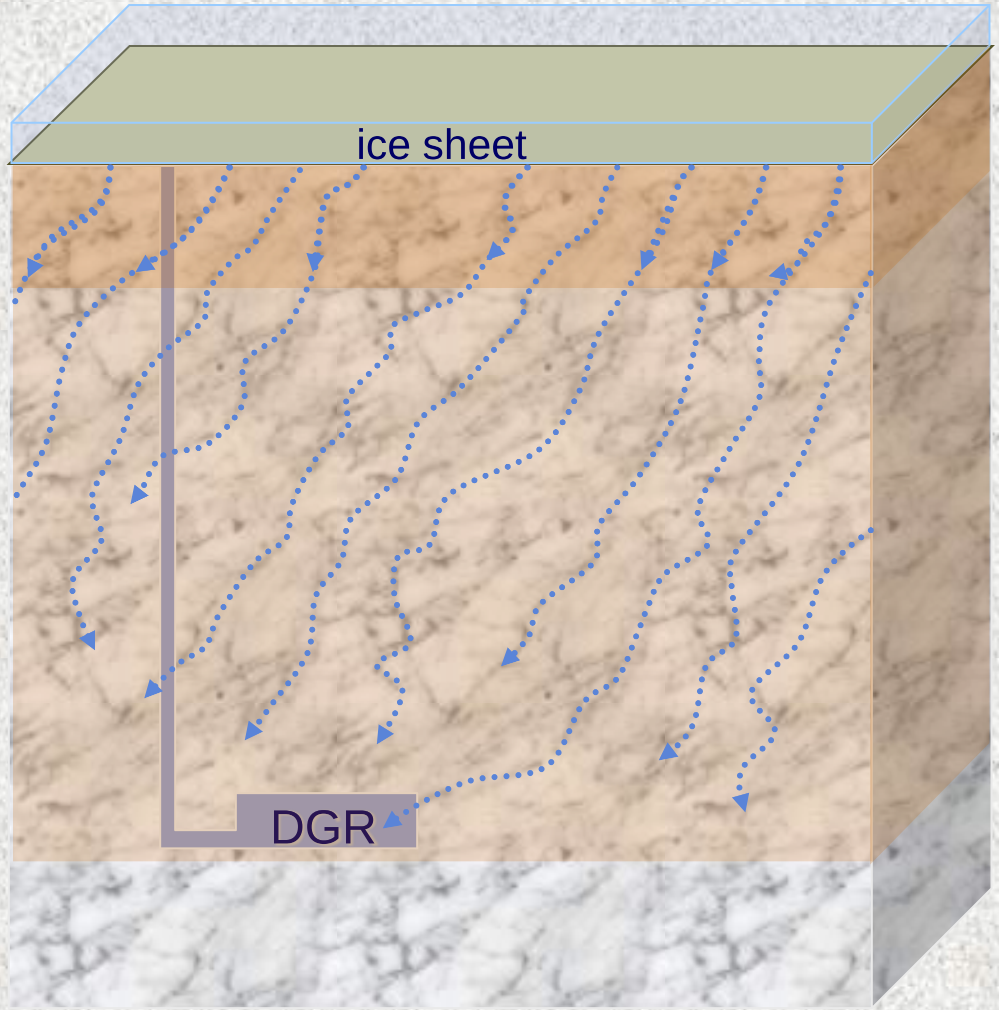
OBJECTIVES

- Investigate solute transport and reaction processes
- Radioactive waste
  - Focus on diffusion and reaction processes
  - Development of lab-scale methods
  - Formation-scale natural tracer profiles
- Contaminant hydrogeology – fractured rocks
  - Effect of diffusion on mass distribution
  - Reactions affecting persistence

RADIOACTIVE WASTE MANAGEMENT

Crystalline Rocks: Paleoredox



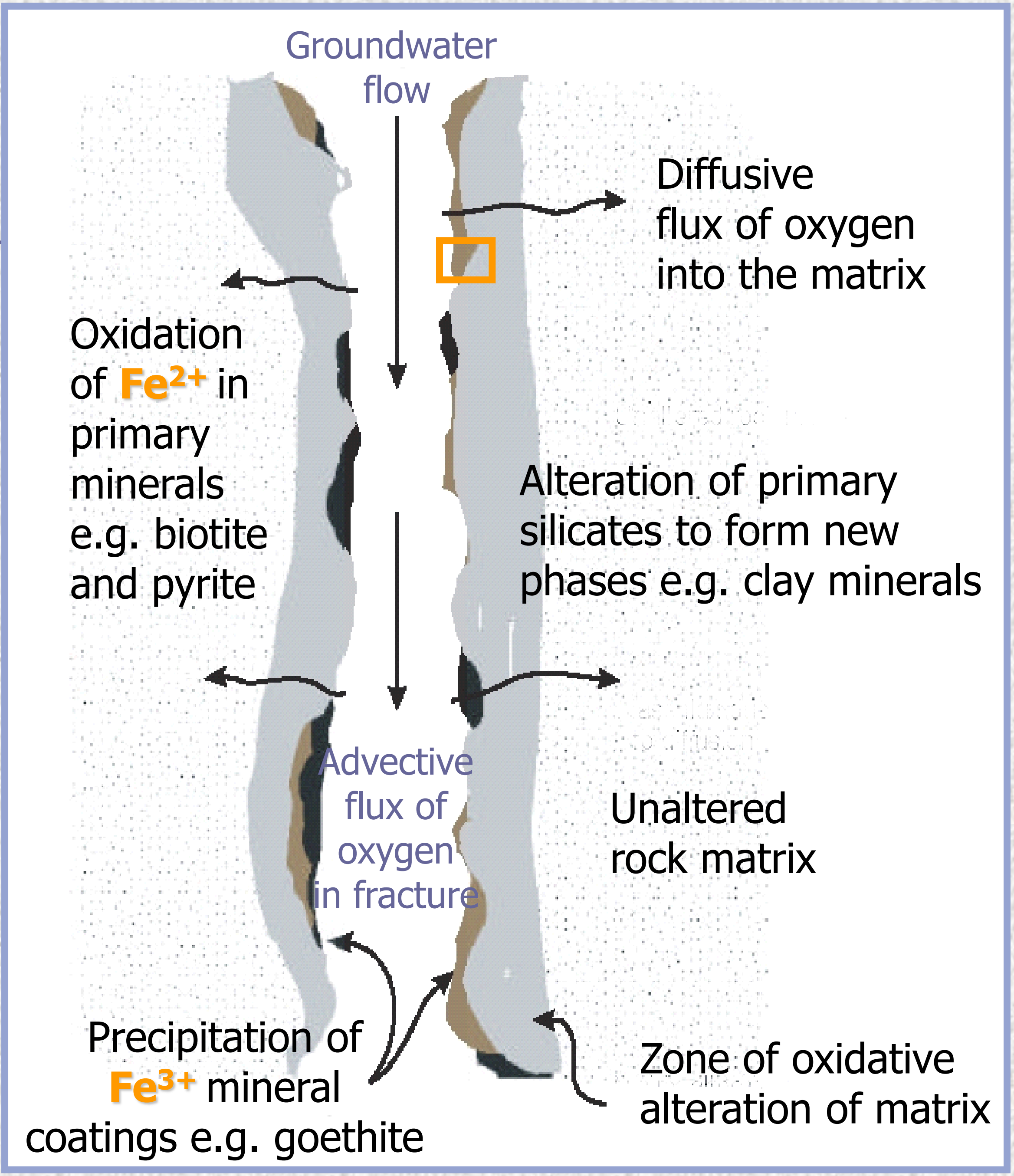
Weathered zone

Oxygenated groundwater

Depth of oxidation?

Fracture

- Conceptual model:
  - Fractured crystalline rock
  - Oxygenated groundwater
  - Mineral reactions



After MacQuarrie & Mayer 2003

Pyrite oxidation

- $FeS_2 + {}^{7}/_{2}\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$

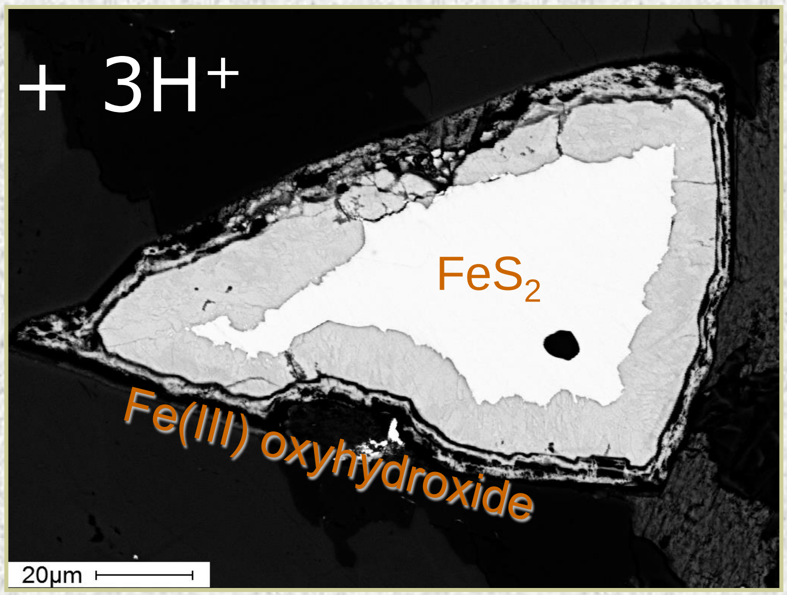
  pyrite

- $Fe^{2+} + {}^{1}/_{4}\ O_2 + H^+ \rightarrow Fe^{3+} + {}^{1}/_{2}H_2O$

- $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$

  iron (III) oxy-hydroxides

After Singer and Stumm, 1970



SEM backscattered electron image

Biotite weathering

$K_2(Mg,Fe^{2+})_3AlSi_3O_{10}(OH)_2$	**biotite**
↓	↓
$(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$ *$Fe^{3+}OOH$*	**interstratified phases** **vermiculite** *goethite*
↓	↓
$Fe^{3+}OOH$ $Al_2Si_2O_5(OH)_4$ *$Al(OH)_3$*	**goethite** **kaolinite** *interstratified phases* *gibbsite*
↓	↓
$Fe^{3+}OOH$ $Al_2Si_2O_5(OH)_4$ *$Al(OH)_3$*	**goethite** **kaolinite** *gibbsite*

increasing weathering ↓

After Gilkes and Suddhiprakarn, 1979

Paleoredox indicators

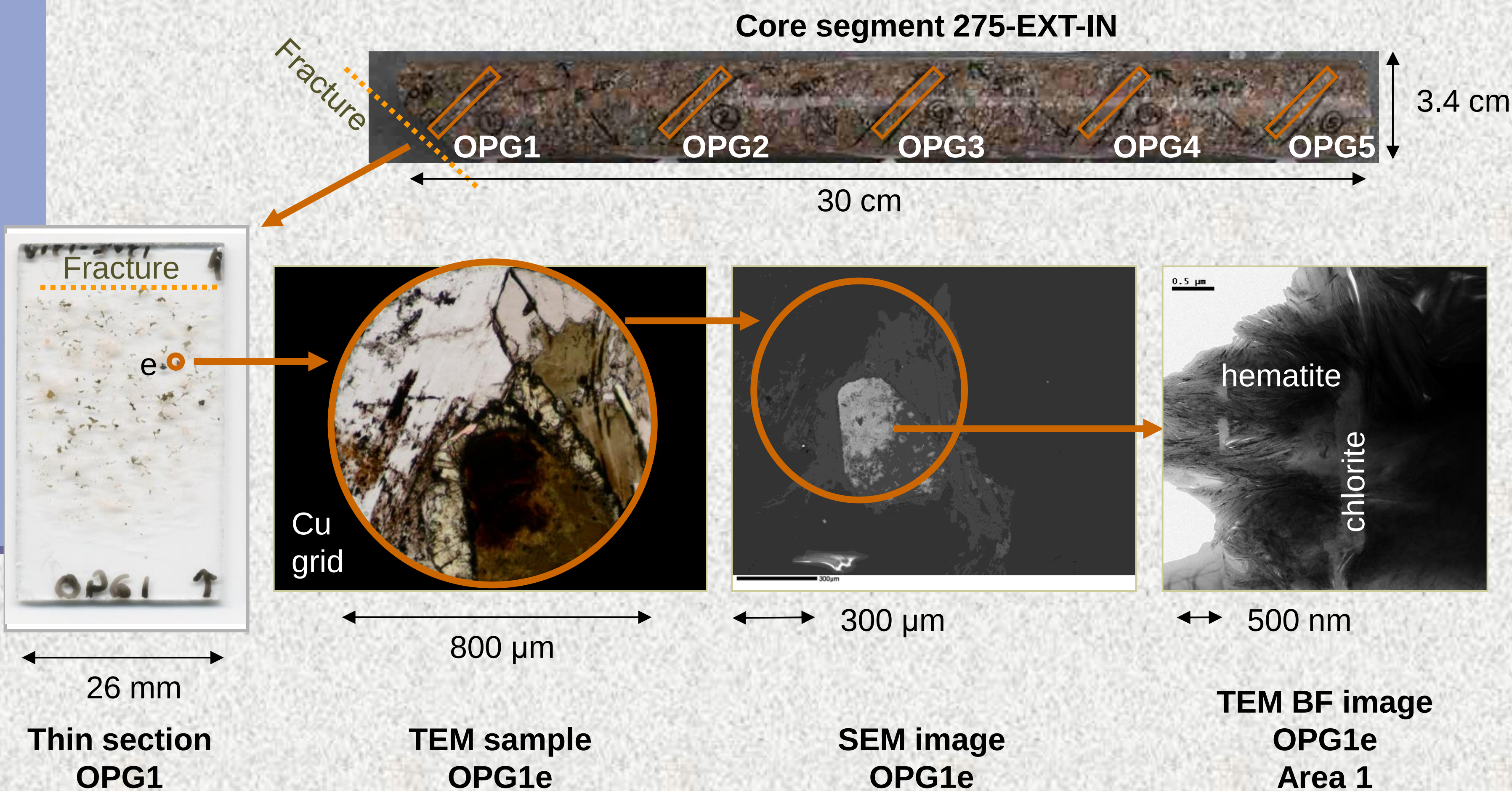
- BIOTITE
  - Slow reactions
  - Phyllosilicate & oxyhydroxide products
  - Irreversible
  - Longer-duration oxidation
- Persistent indicator

- PYRITE
  - Fast reactions
  - Oxyhydroxide products
  - Removable by reduction
  - Shorter-duration oxidation
- Sensitive indicator

Drill core samples - Whiteshell

Depth below surface (m)	Sample(s) on fracture	Sample(s) away from fracture	Comments
~7	OPG0	-	Weathered sample on shallow fracture.
~15	OPG1, 1A, 1B	OPG2, 3, 4, 5	Sequence of samples versus distance from fracture
~65	OPG6	OPG7	Thin section intersects 2 fracture faces
~135	OPG14	OPG15	Coarse grained fractured granite
~170	OPG11, 12	OPG13	Vertical NE fracture 2 fracture faces
~240	OPG8, 9	OPG10	Vertical NE fracture
~240	-	OPG16	Unfractured pink granite
~240	-	OPG17	Unfractured grey granite

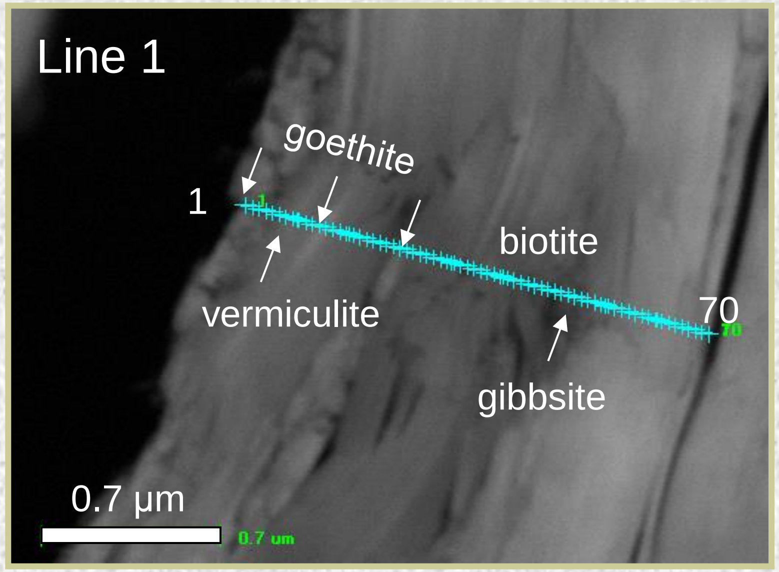
Approach



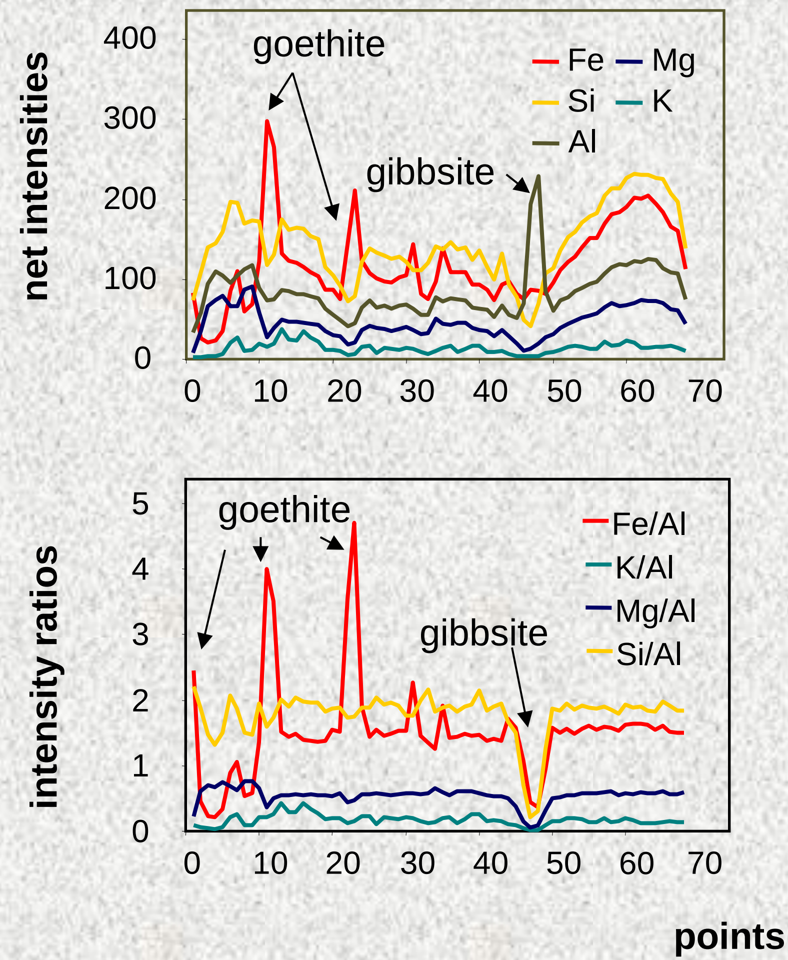
Core segment 275-EXT-IN
Fracture
OPG1
OPG2
OPG3
OPG4
OPG5
3.4 cm
30 cm
Fracture
e
OPG1
Cu
grid
hematite
chlorite
0.5 µm
300µm
26 mm
800 µm
300 µm
500 nm
Thin section
OPG1
TEM sample
OPG1e
SEM image
OPG1e
TEM BF image
OPG1e
Area 1

~ 7 m depth

Shallow fracture



STEM ADF image

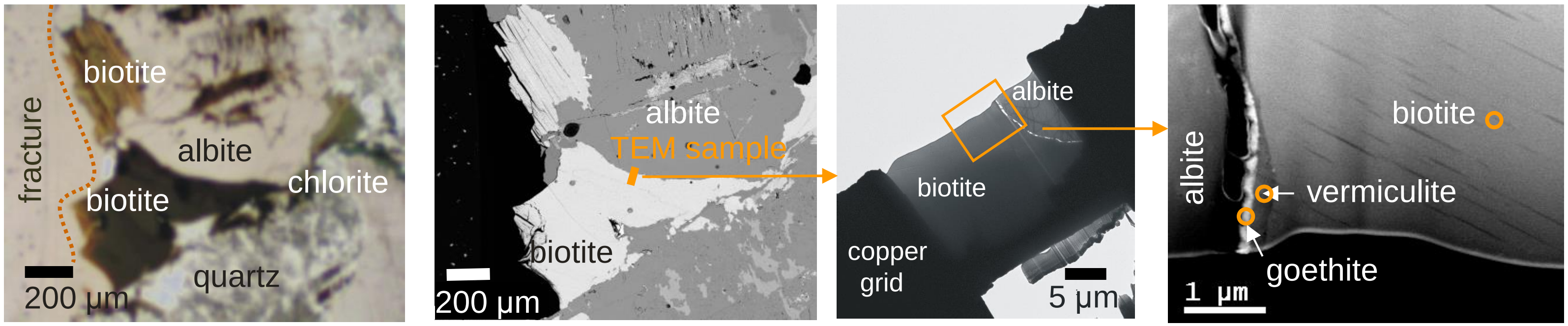


STEM-EDS multipoint line scans

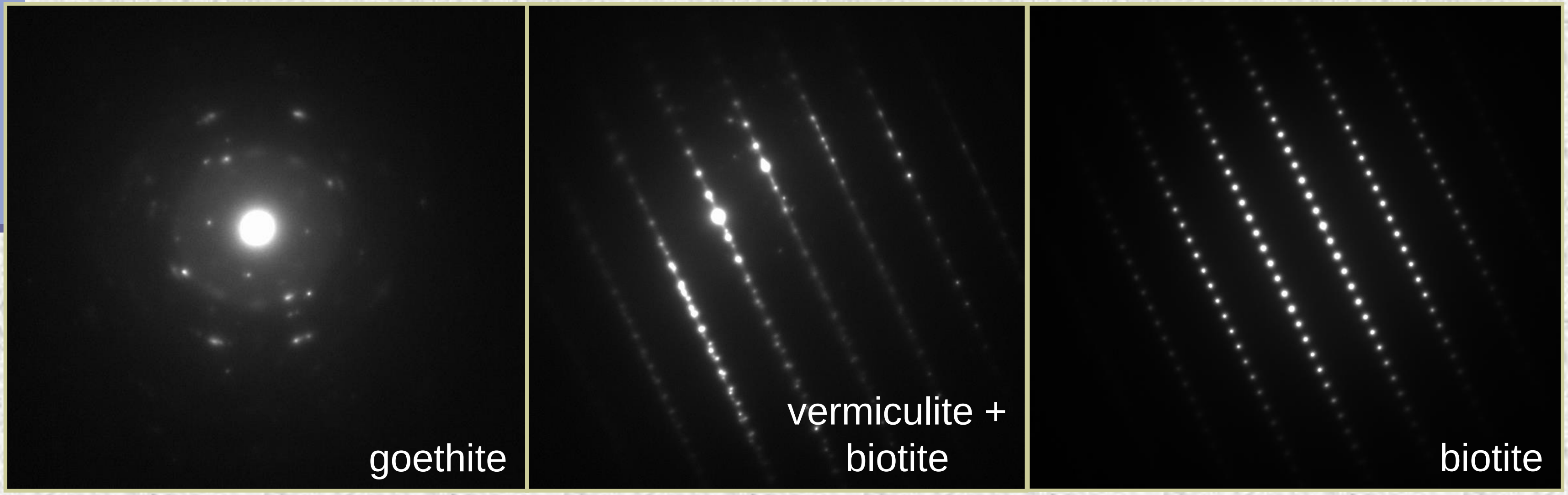
Biotite weathering products

~ 7 m depth

Shallow fracture



Thin section SEM BSE image TEM sample STEM ADF image

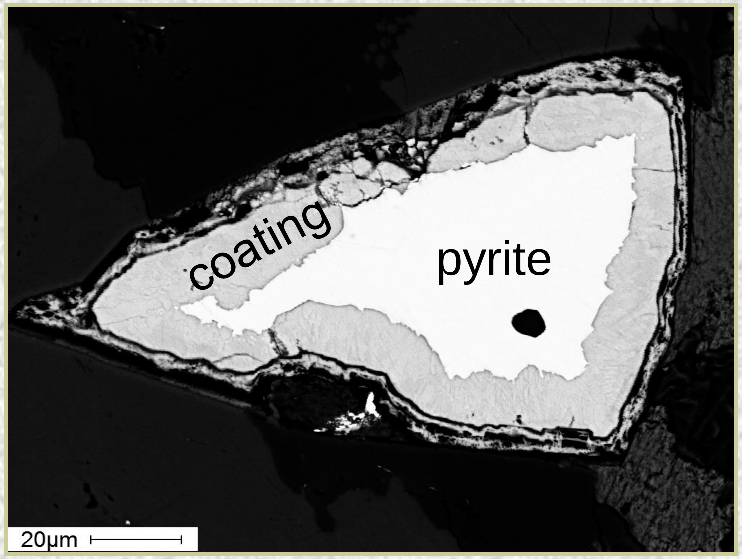


TEM ED patterns

~ 7 m depth

Evidence of oxidizing groundwater

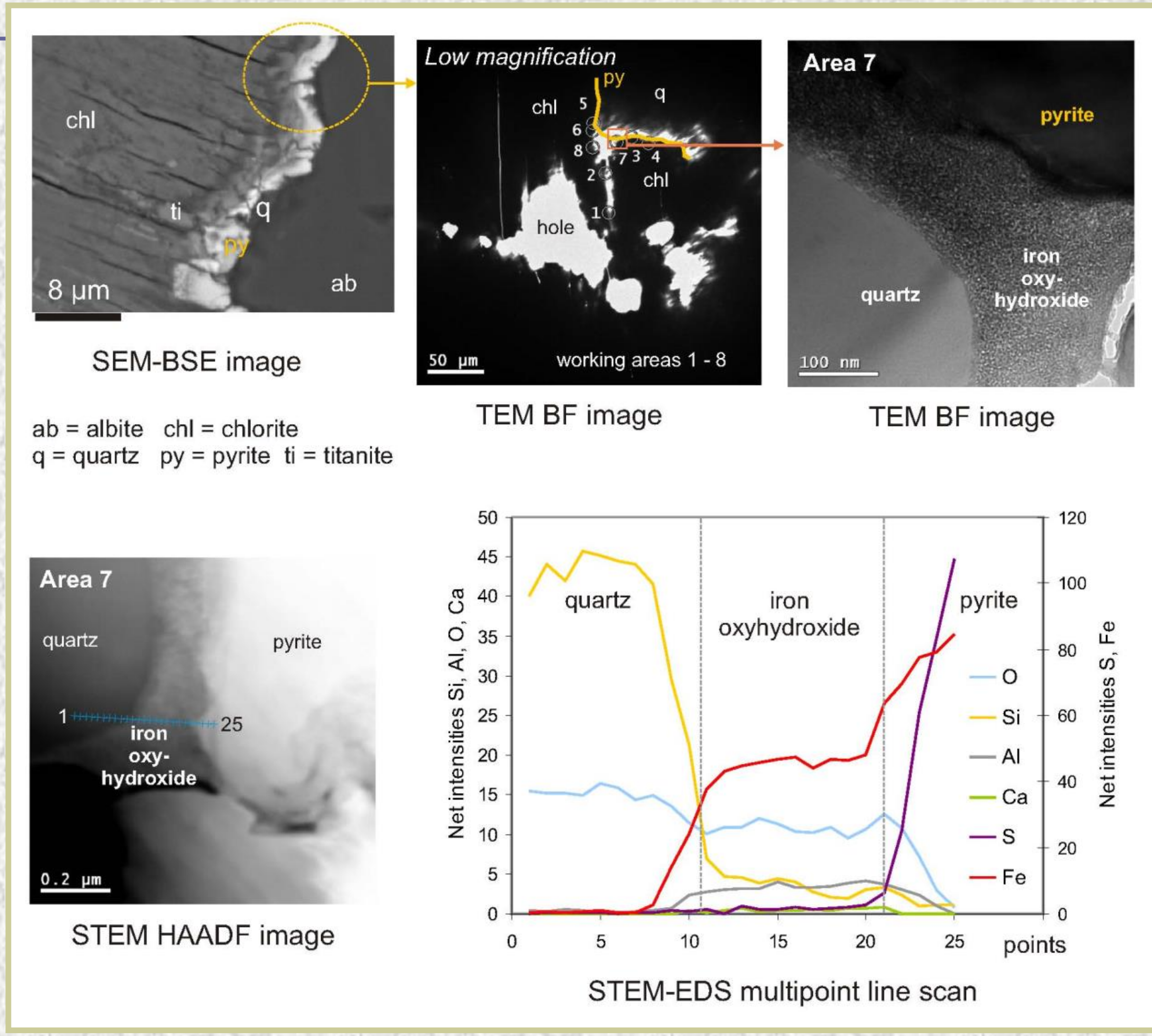
- Optical:
  - brown regions on fracture edge of biotite
- SEM-BSE:
  - Fe oxyhydroxide coating on pyrite
- TEM:
  - biotite weathering products:
    - vermiculite, kaolinite, goethite and gibbsite
    - 100 to 150 nm goethite along biotite margin



~ 65 m depth

Pyrite oxidation

Evidence of oxidizing groundwater



SEM-BSE image

TEM BF image

TEM BF image

STEM HAADF image

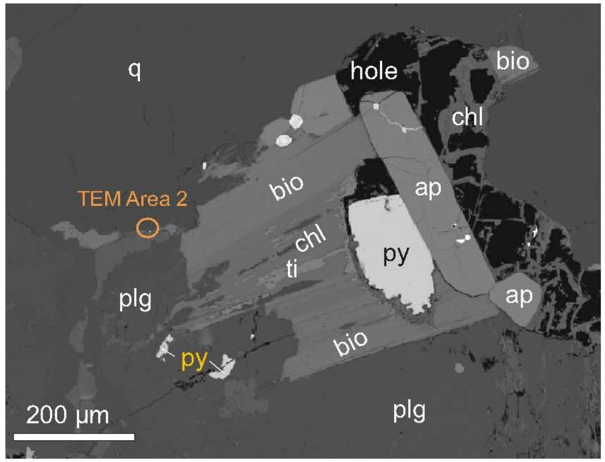
STEM-EDS multipoint line scan

Pyrite oxidation products

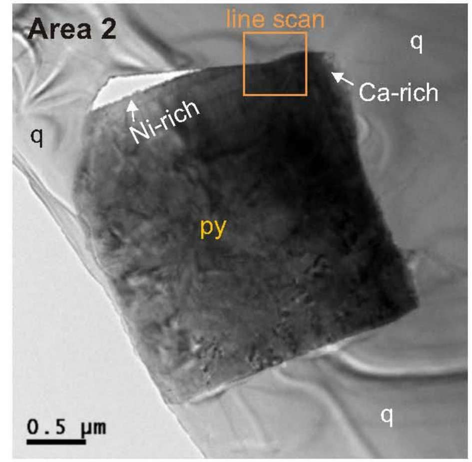
~170 m depth

Unreacted pyrite

Deep fractures

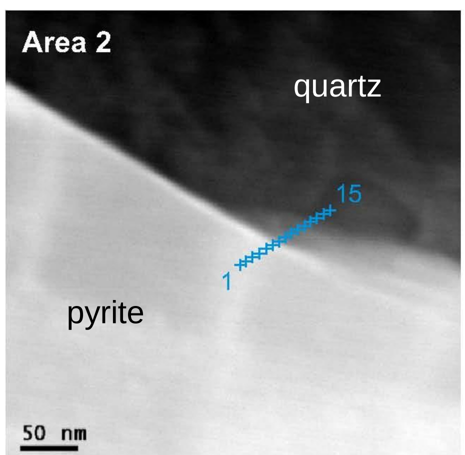


SEM BSE image

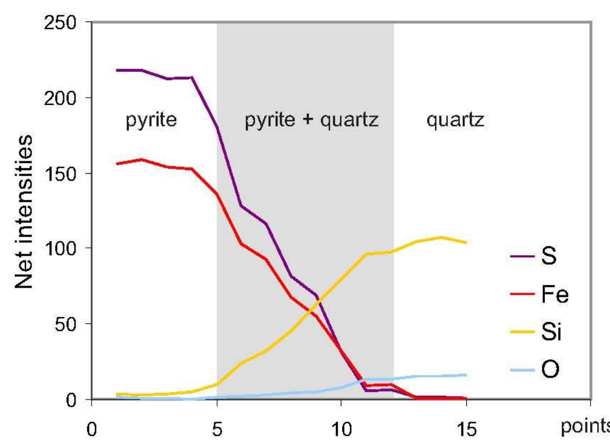


TEM BF image

ap = apatite bio = biotite chl = chlorite plg = plagioclase py = pyrite q = quartz ti = titanite



STEM-ADF image



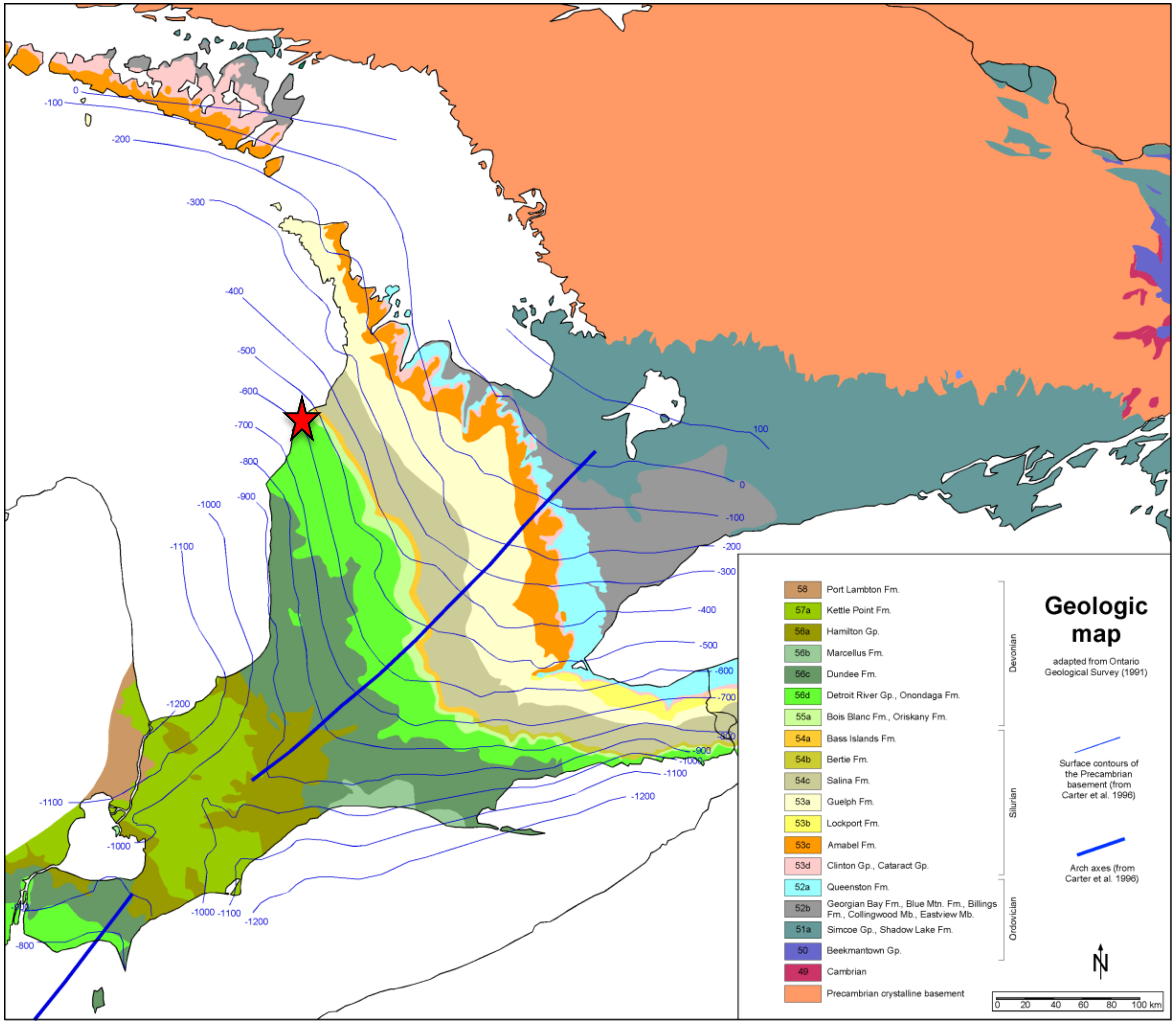
STEM-EDS multipoint line scan

No pyrite oxidation products

Synthesis

Depth	Evidence	Deductions
Shallow (0 – 7 m)	Weathered biotite Oxidized pyrite (20 μm)	Extended contact with O_2 in groundwater
Intermediate (15 – 65 m)	Unreacted biotite Oxidized pyrite (<100 nm)	Brief contact with O_2 in groundwater
Deep (135 – 240 m)	Unreacted biotite Unreacted pyrite	No contact with O_2 in ground-water

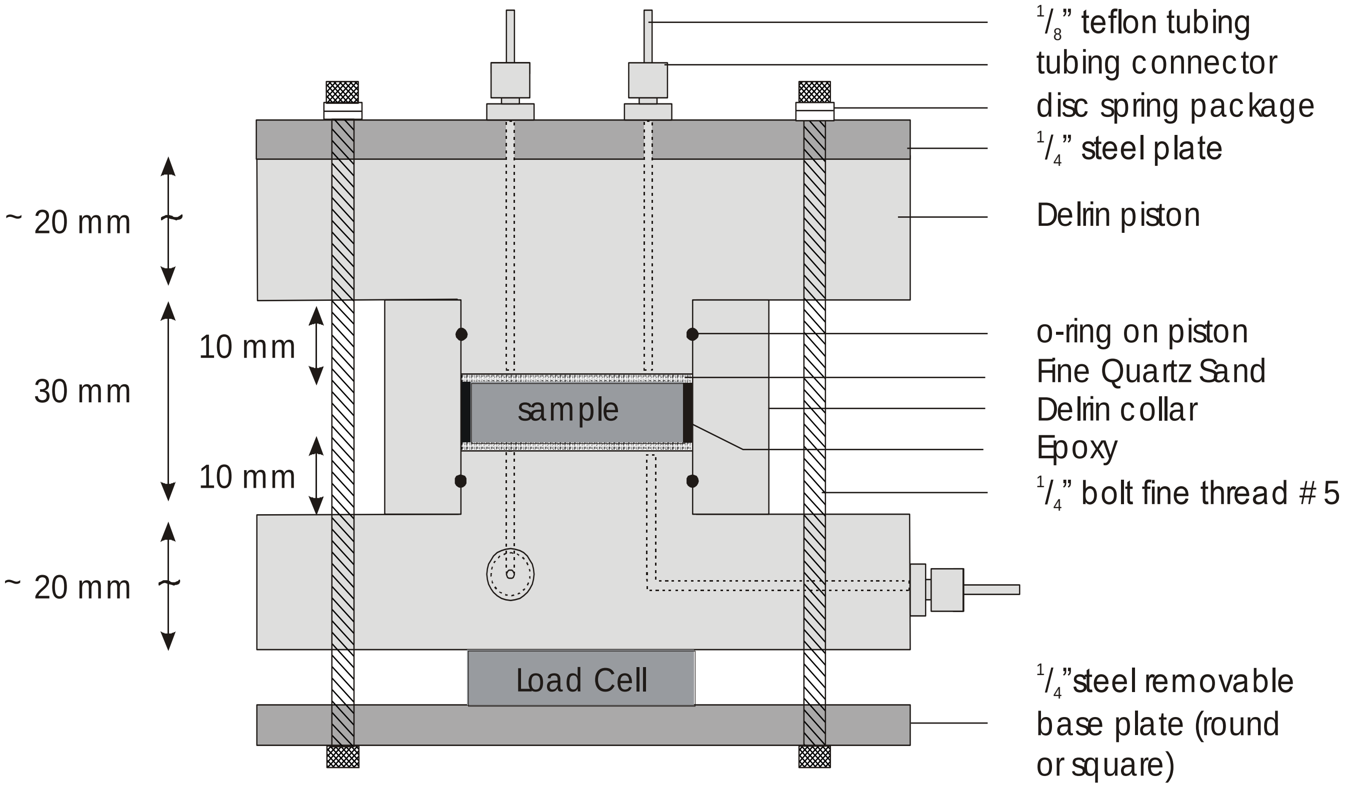
SEDIMENTARY ROCKS: BRUCE DGR
(LOW AND INTERMEDIATE LEVEL WASTE)



LOW-PERMEABILITY ROCKS

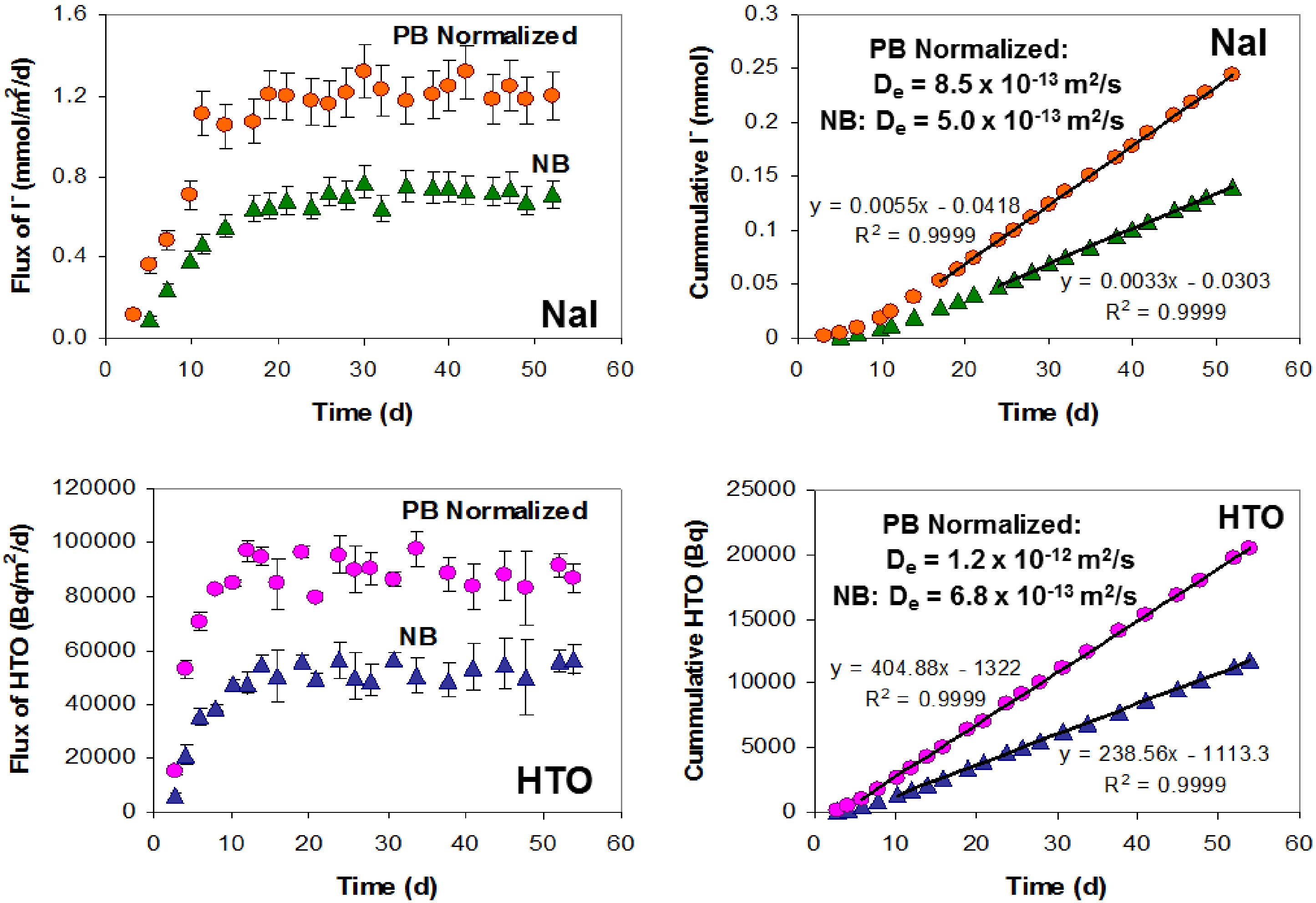
MEASUREMENT METHODS

Through Diffusion



THROUGH-DIFFUSION DATA

DIFFUSIVE ANISOTROPY

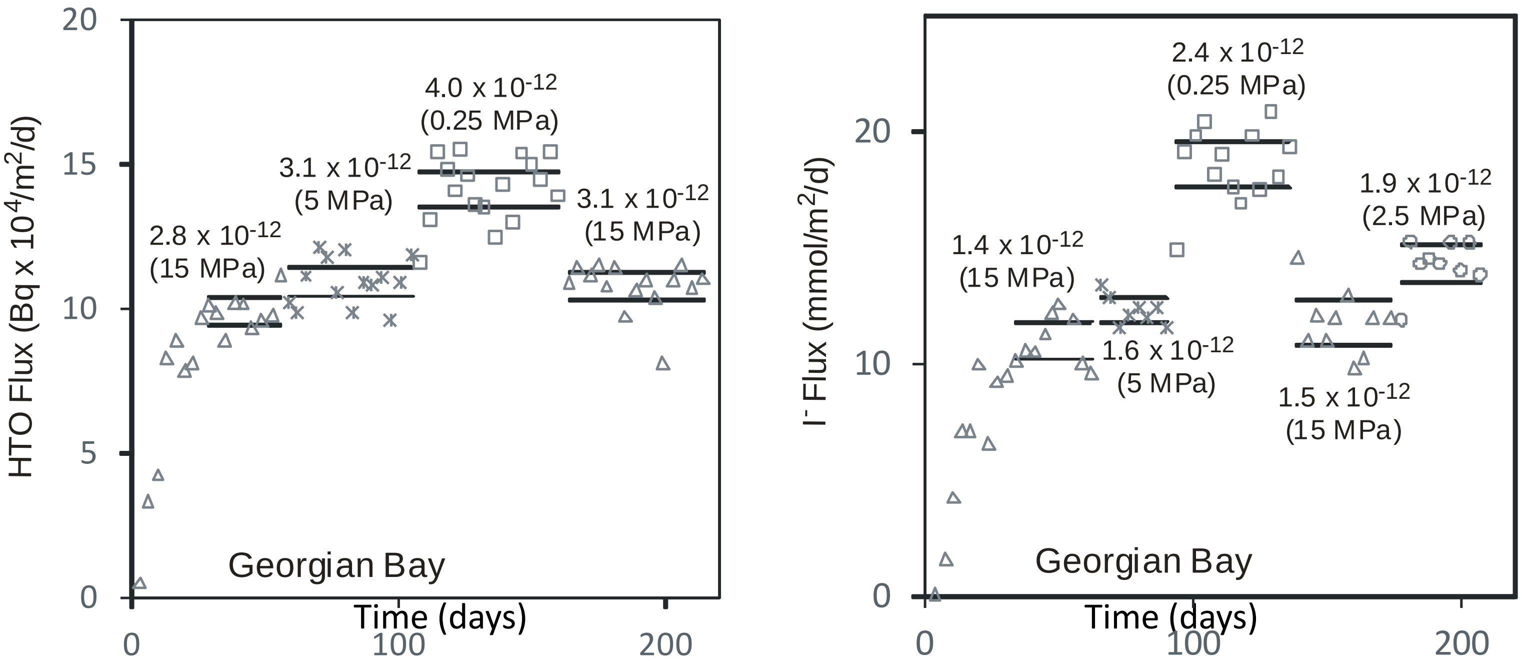


CONFINING PRESSURE

What is the effect of confining pressure on D_e ?

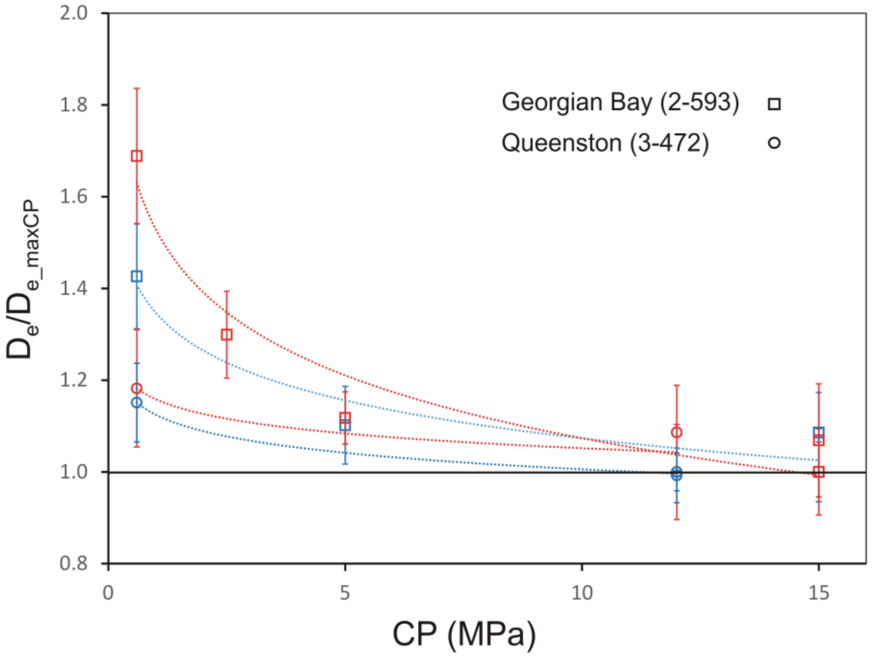
Is it reversible – reproducible in the lab?

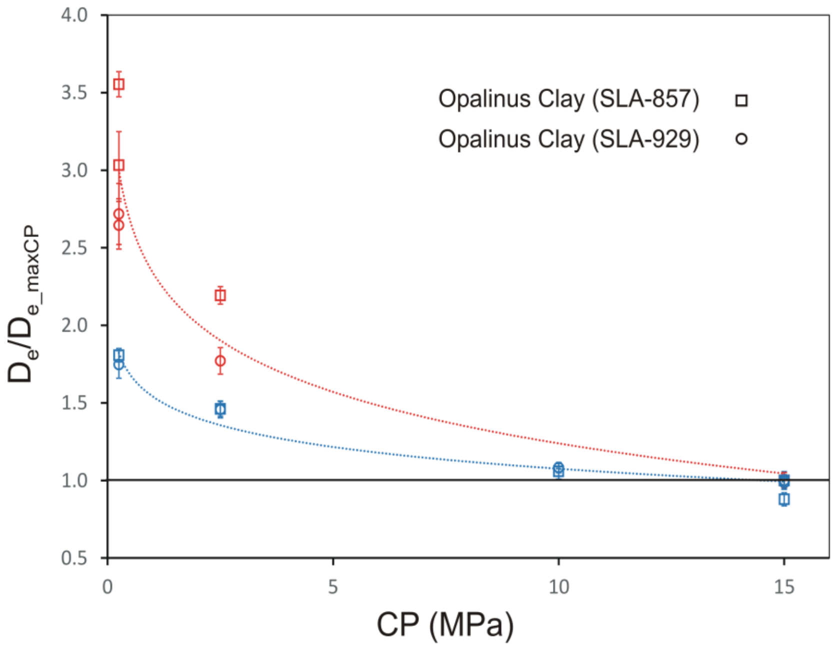
Is it predictable?



CONFINING PRESSURE

It is it reversible – for clay-rich rocks

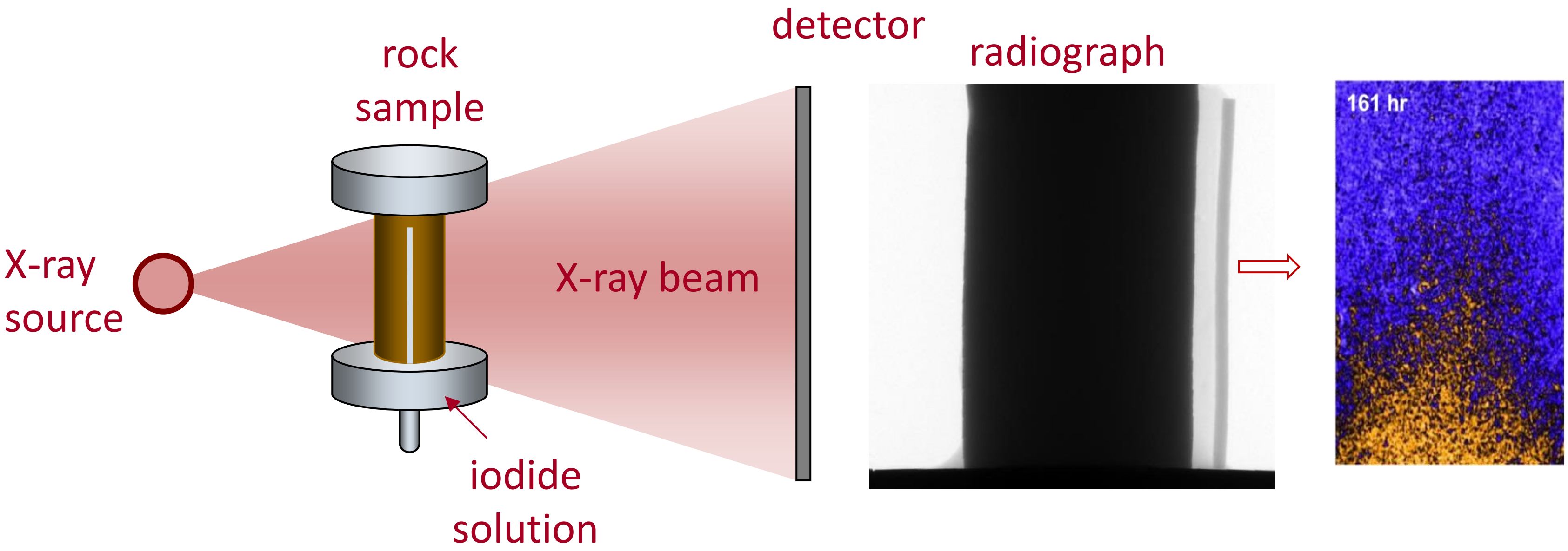




MEASUREMENT METHODS

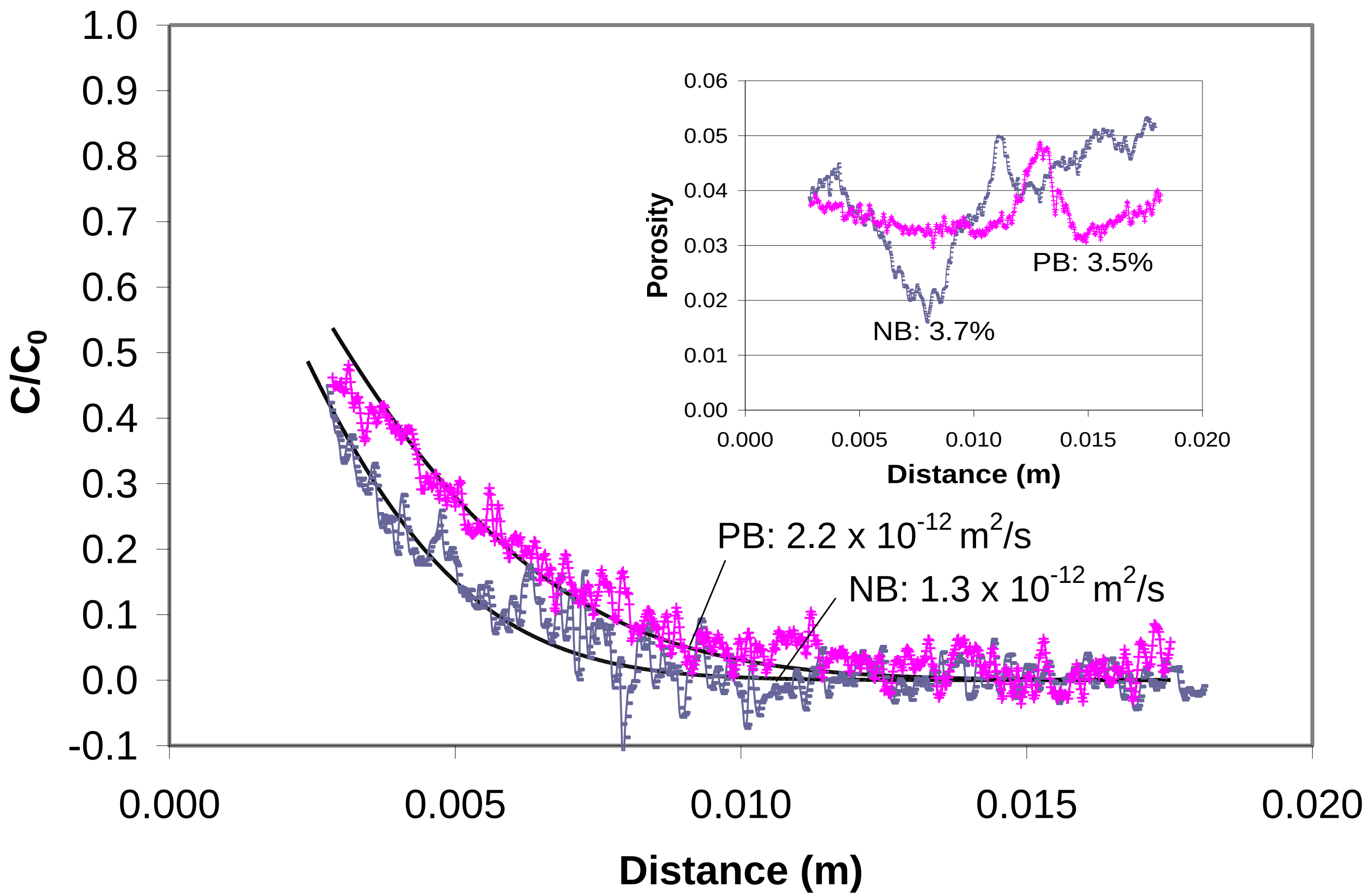
Radiography

- Non-destructive measurements
- X-ray absorbing tracers

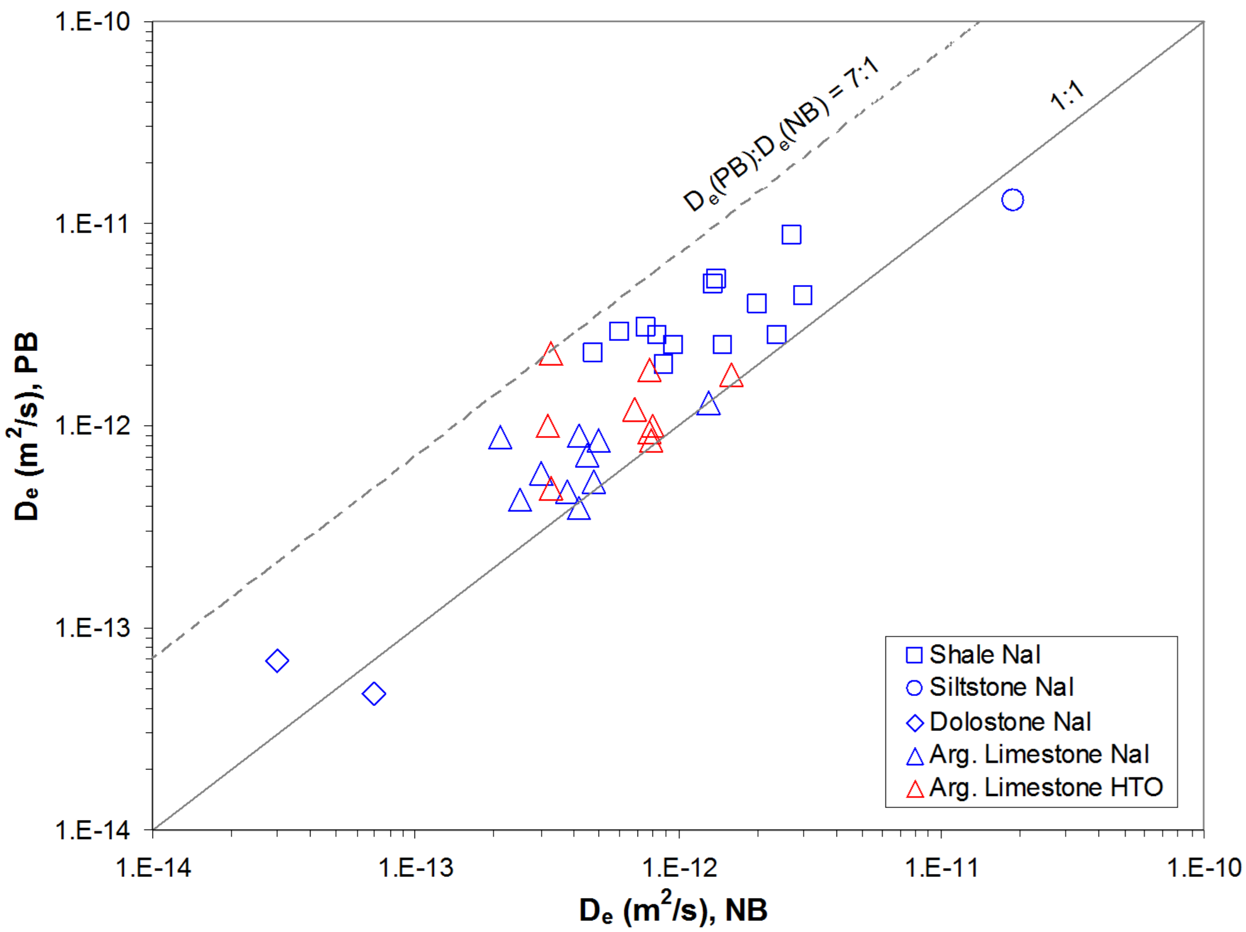


RADIOGRAPHY DATA

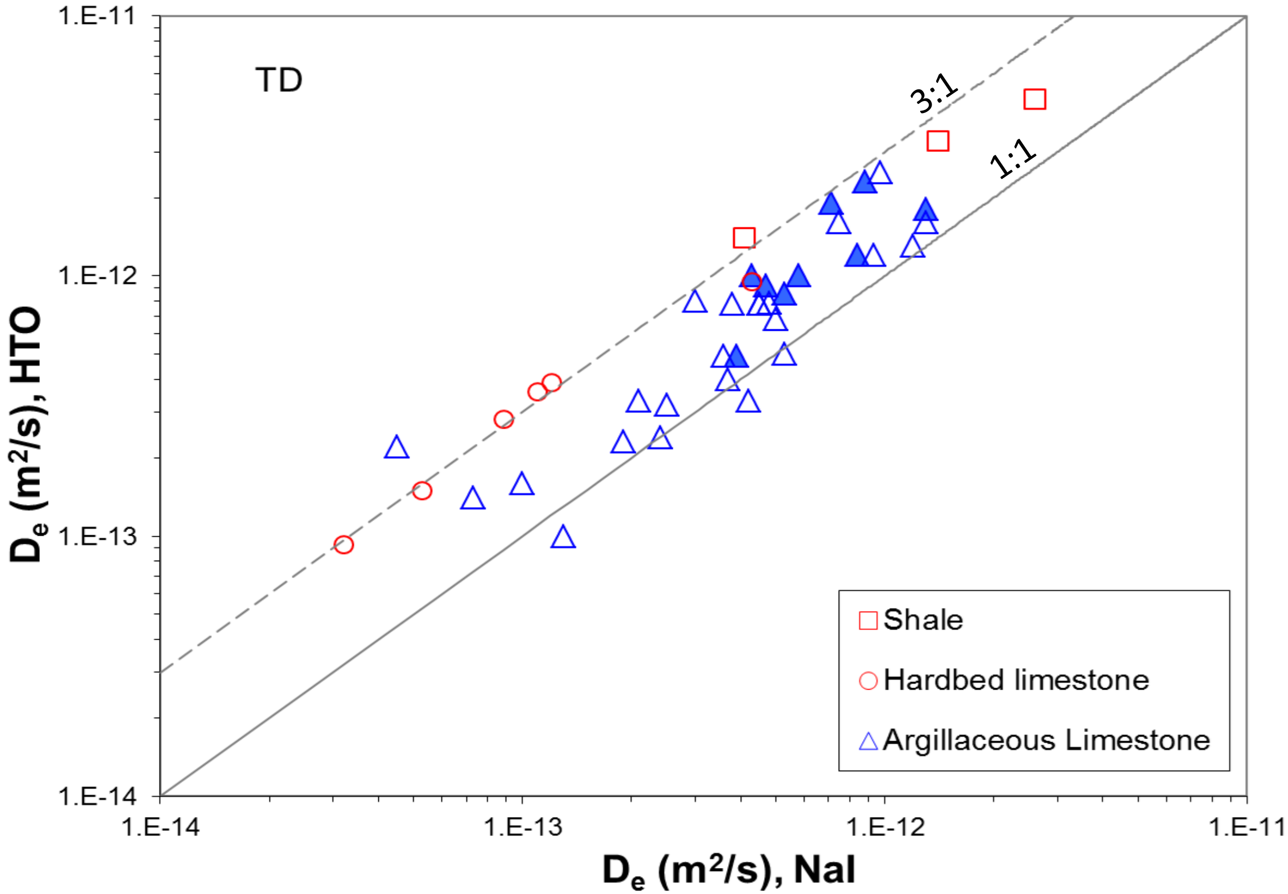
DIFFUSIVE ANISOTROPY



ANISOTROPY: RADIOGRAPHY AND THROUGH DIFFUSION

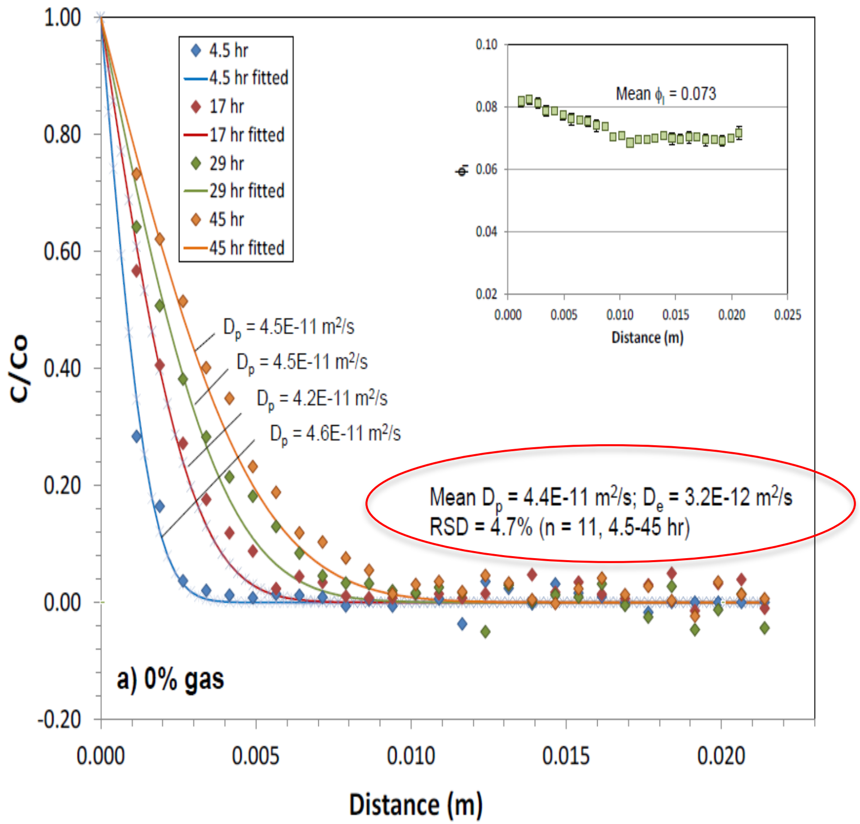


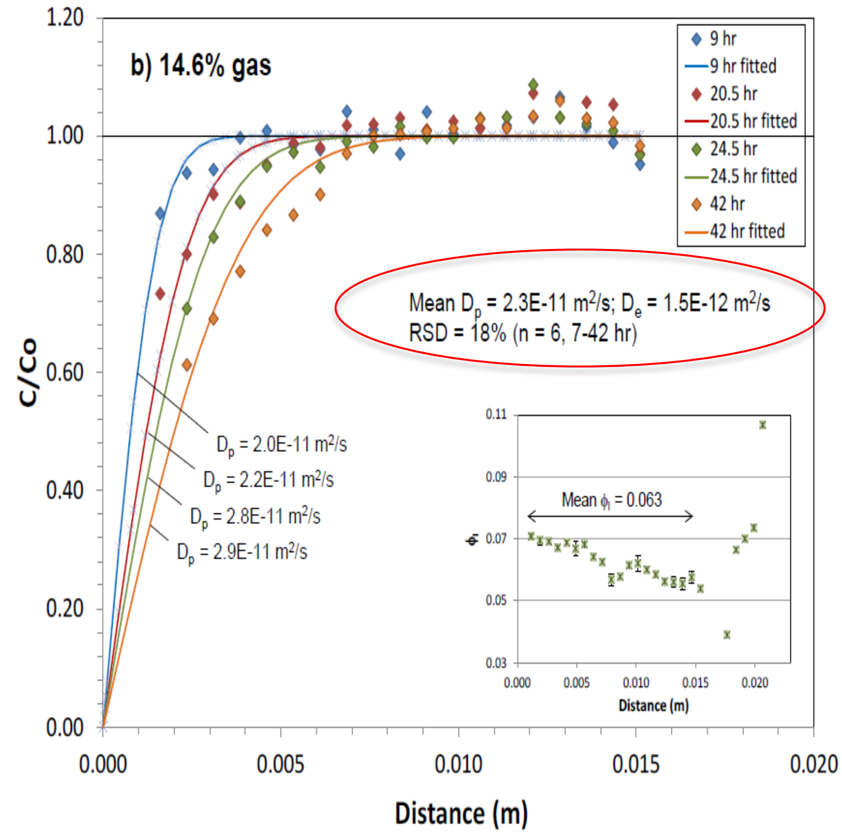
TRACER-SPECIFIC PROPERTIES:
RADIOGRAPHY AND THROUGH DIFFUSION



PARTIAL GAS SATURATION

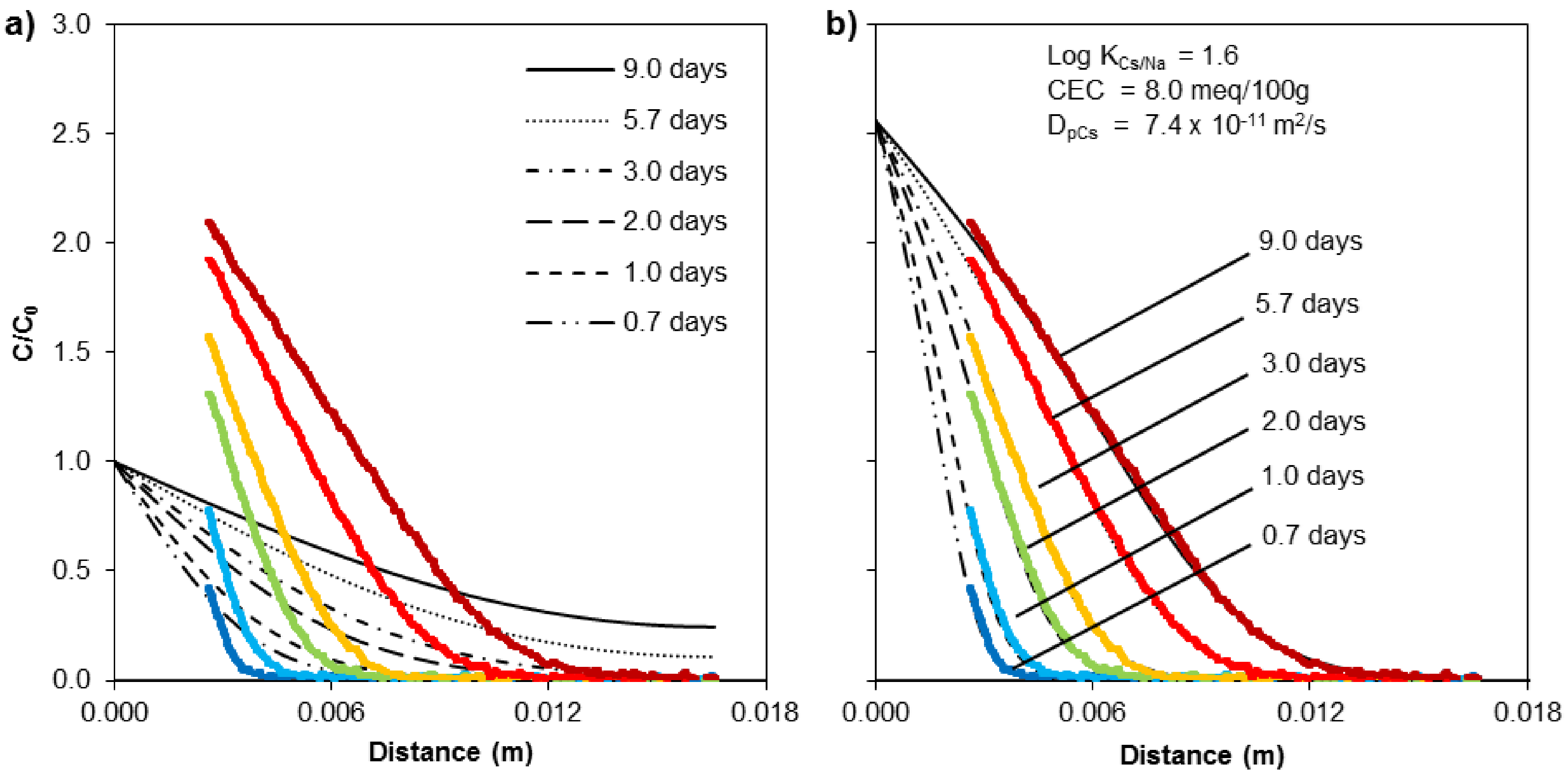
RADIOGRAPHY - QUEENSTON SHALE



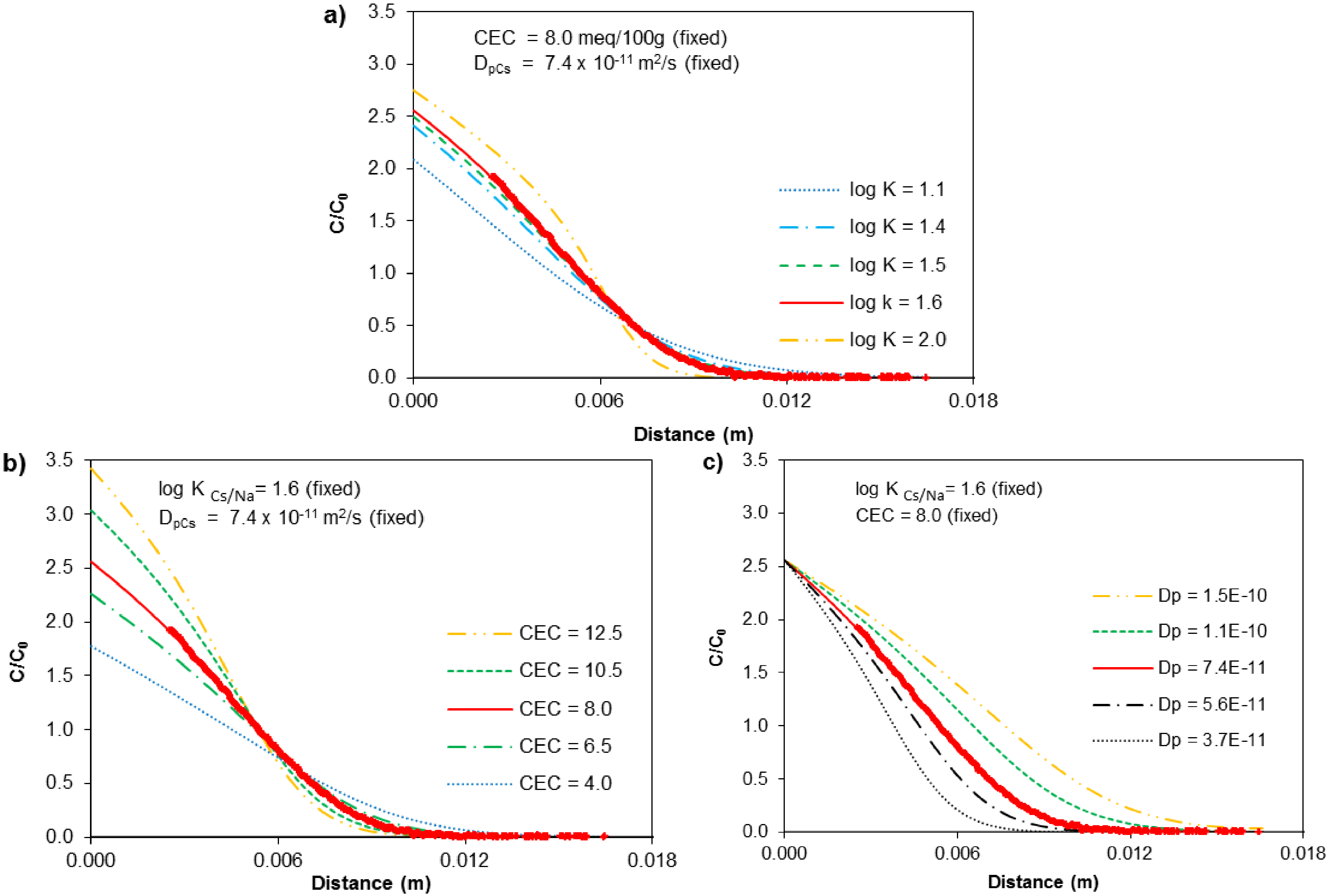


REACTIVE TRANSPORT

RADIOGRAPHY - DIFFUSION / REACTION - Cs

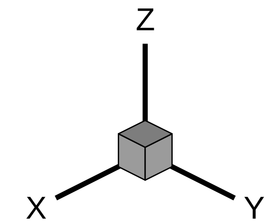


REACTIVE TRANSPORT

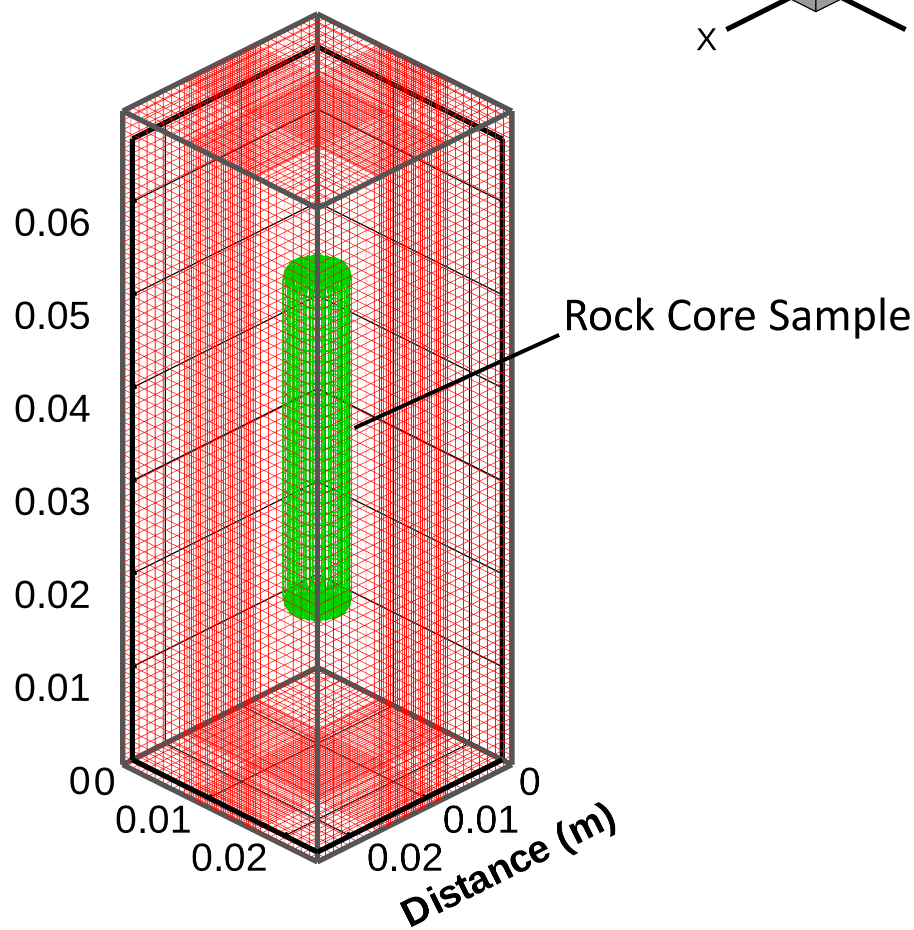


GAS DIFFUSION: He OUT-DIFFUSION EXPERIMENTS

- Goal is to estimate residence time by modelling ^{4}He ingrowth coupled to gains/losses by diffusion

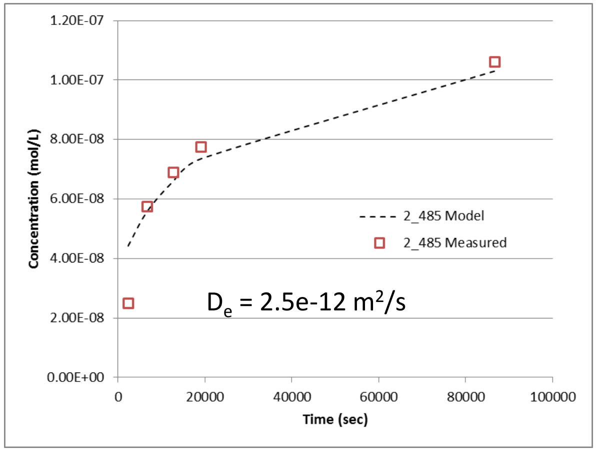


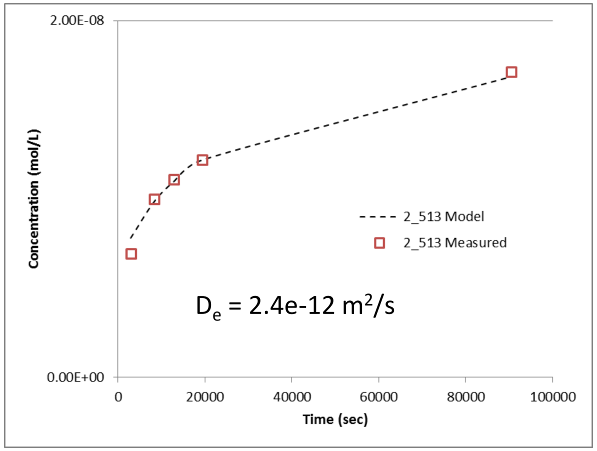
- He diffusion coefficients determined by fitting model to out-diffusion data
- Numerical domain with zero flux enclosing boundary

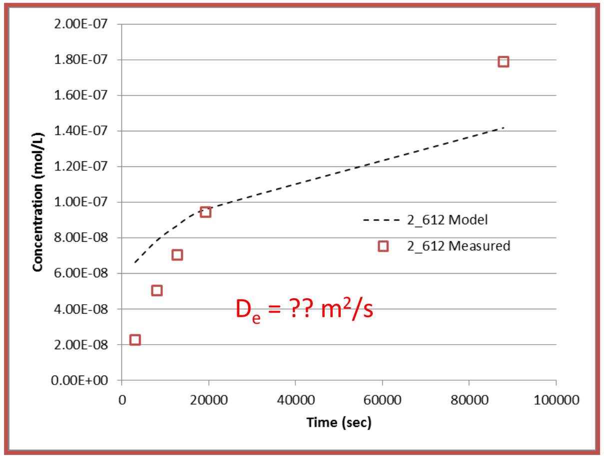


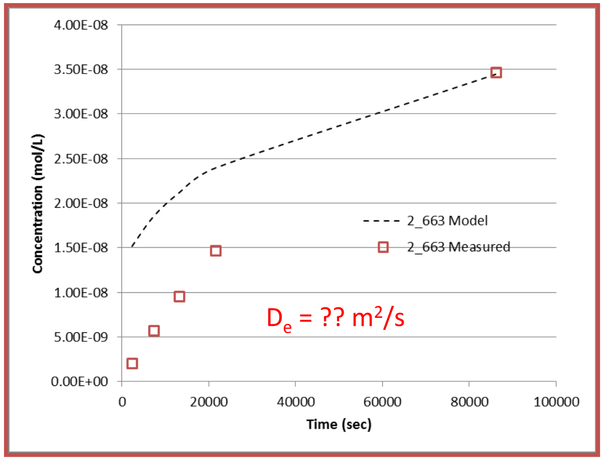
He OUT-DIFFUSION DATA

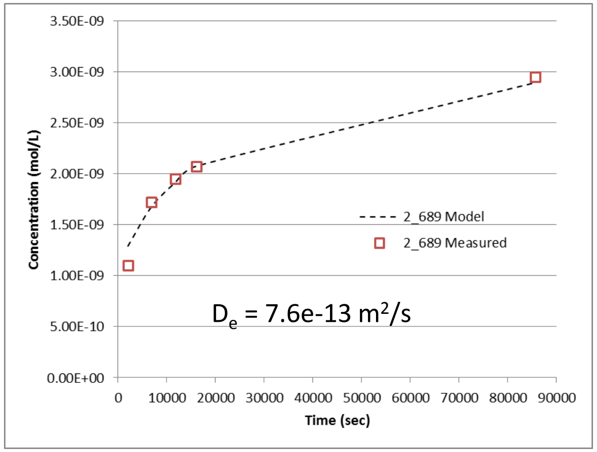
Investigate the influence of organic-rich units on D_{e_He}

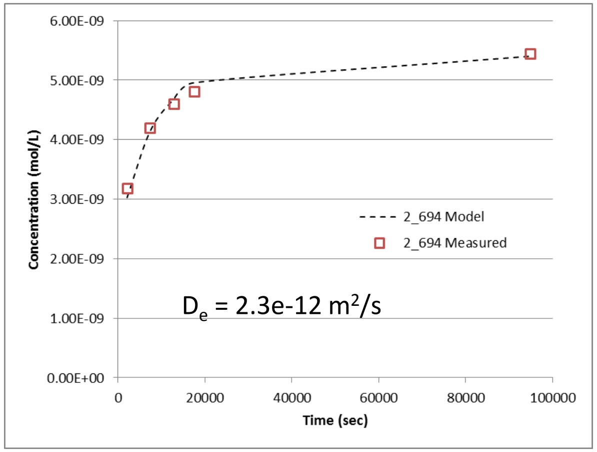




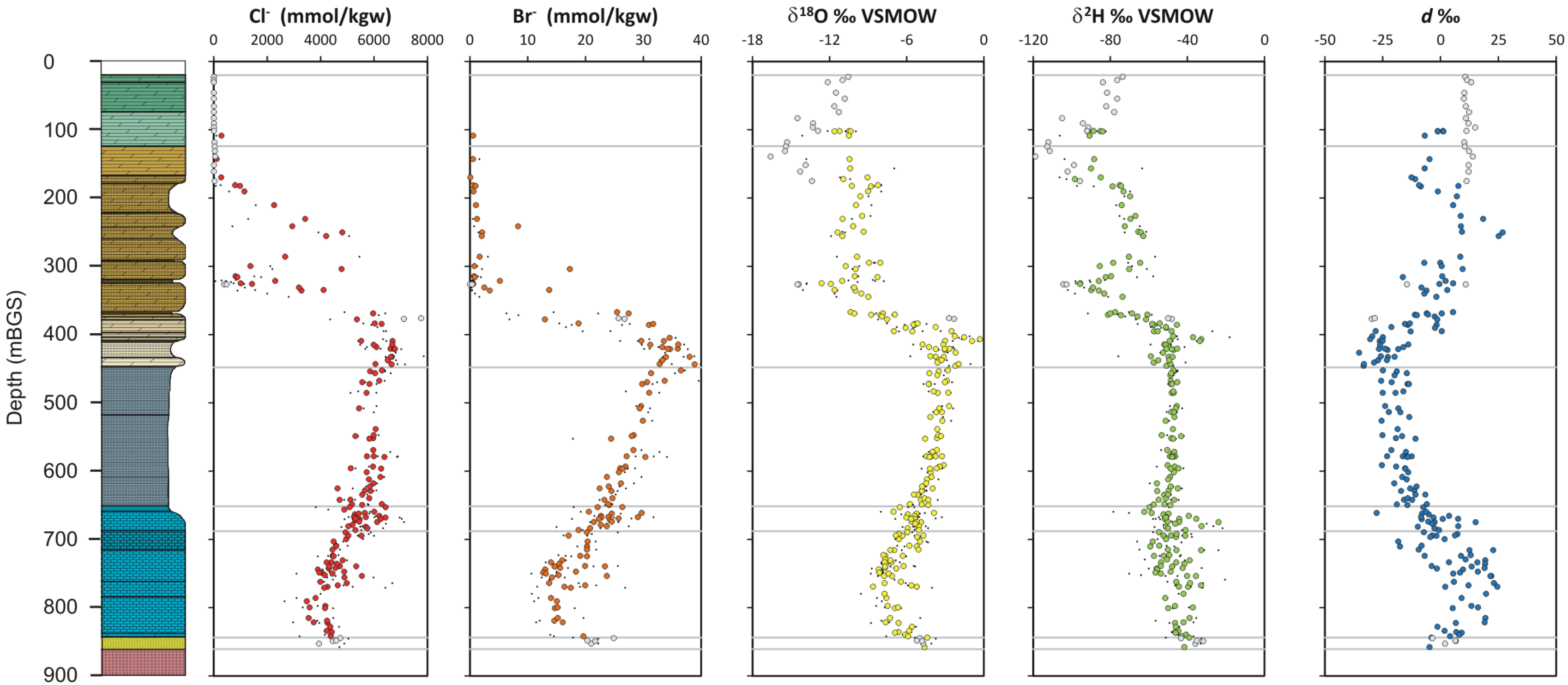




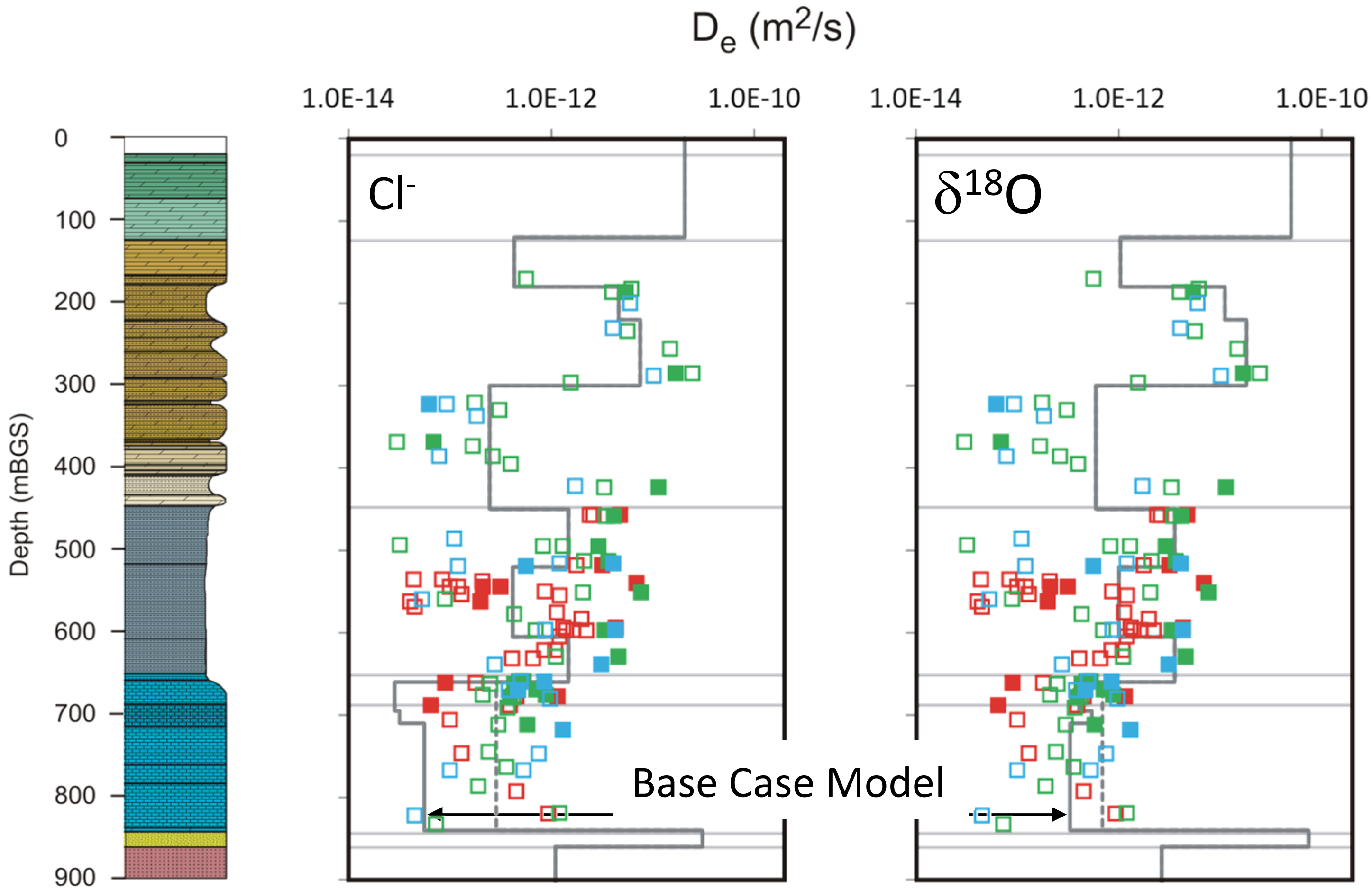




NATURAL TRACERS: SCALING UP

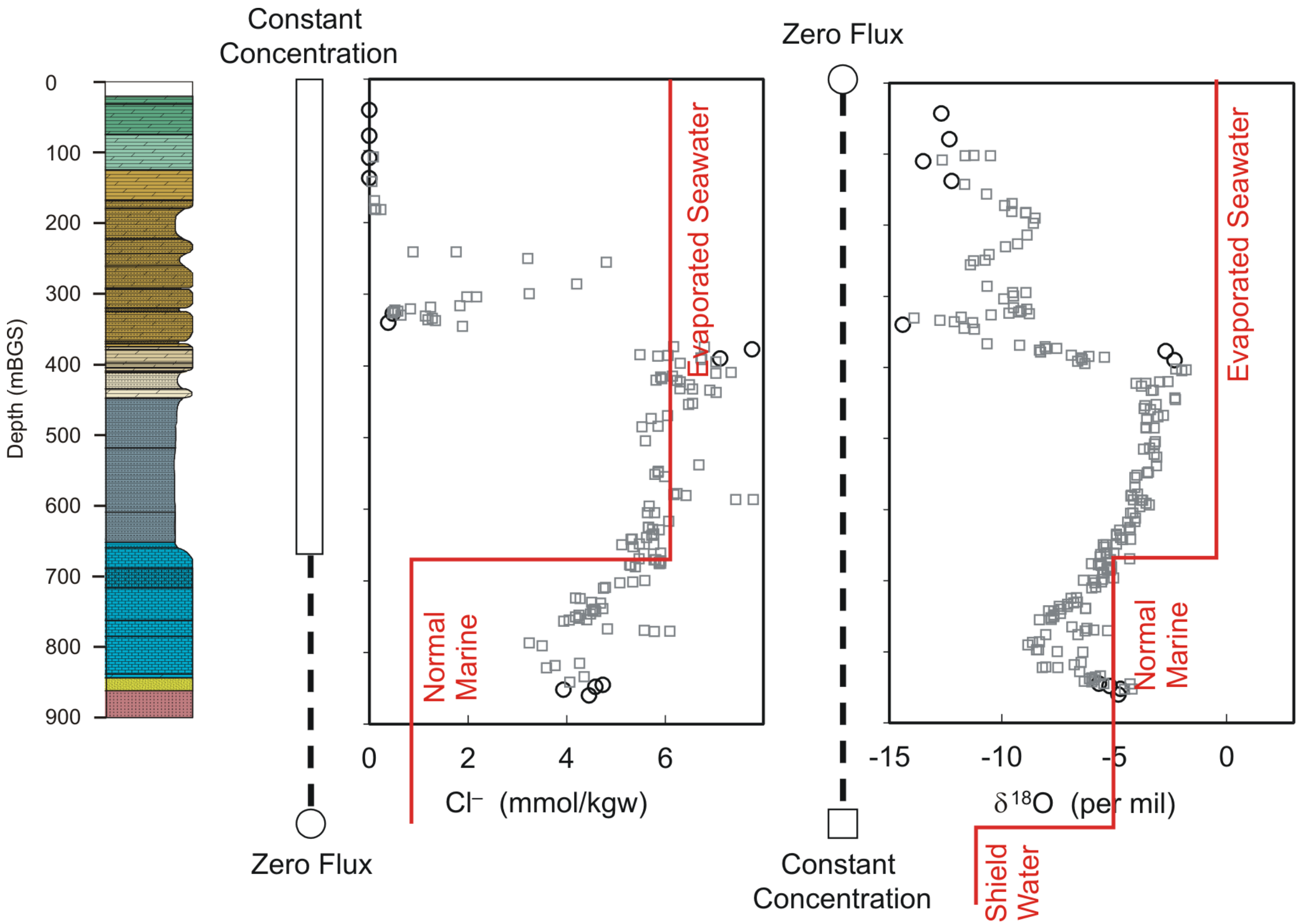


NATURAL TRACERS: SCALING UP



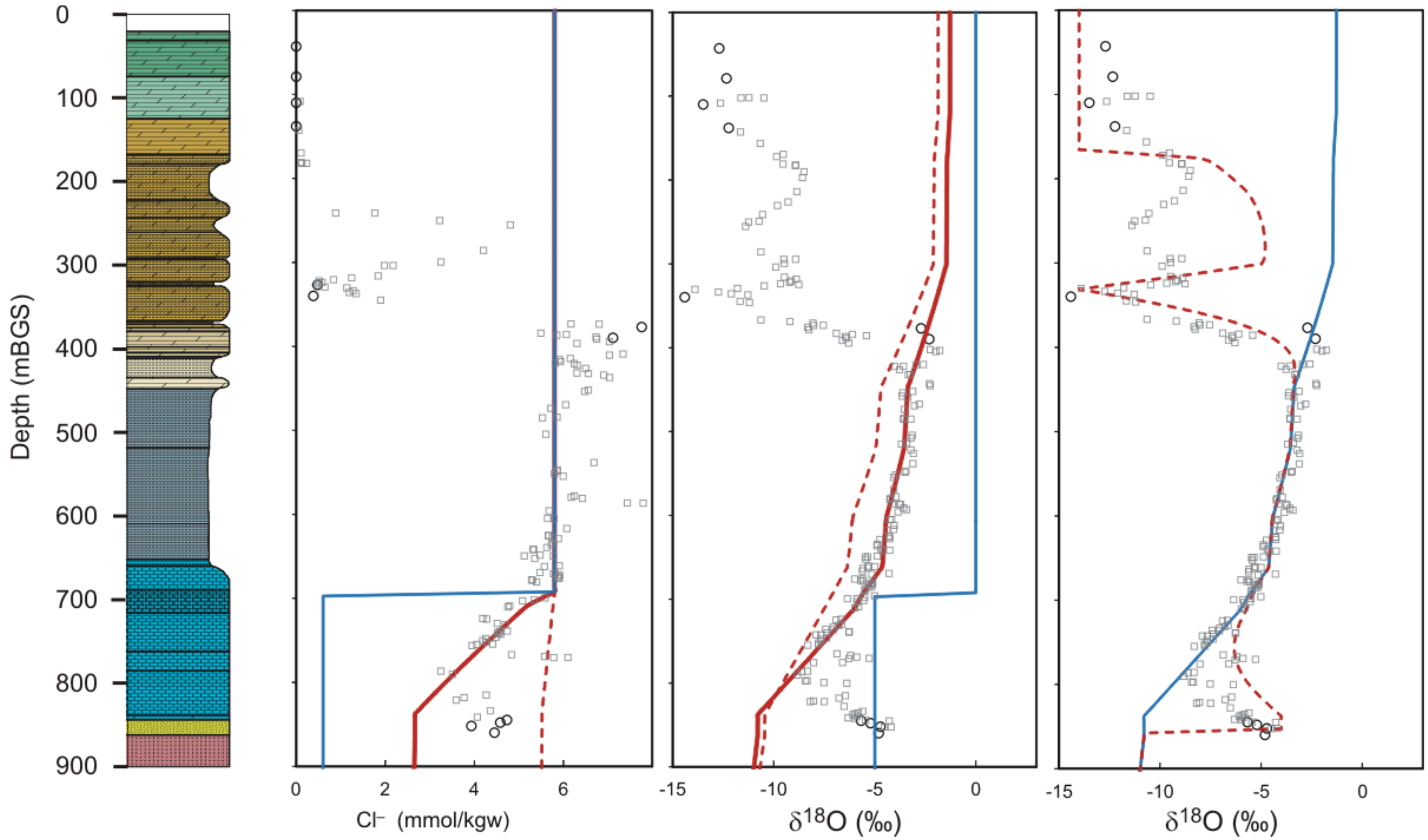
NATURAL TRACERS: SCALING UP

INITIAL AND BOUNDARY CONDITIONS



NATURAL TRACERS: SCALING UP

SIMULATIONS - 300 MA TIME SCALE



CONTAMINANT HYDROGEOLOGY

CHROMIUM EXAMPLE

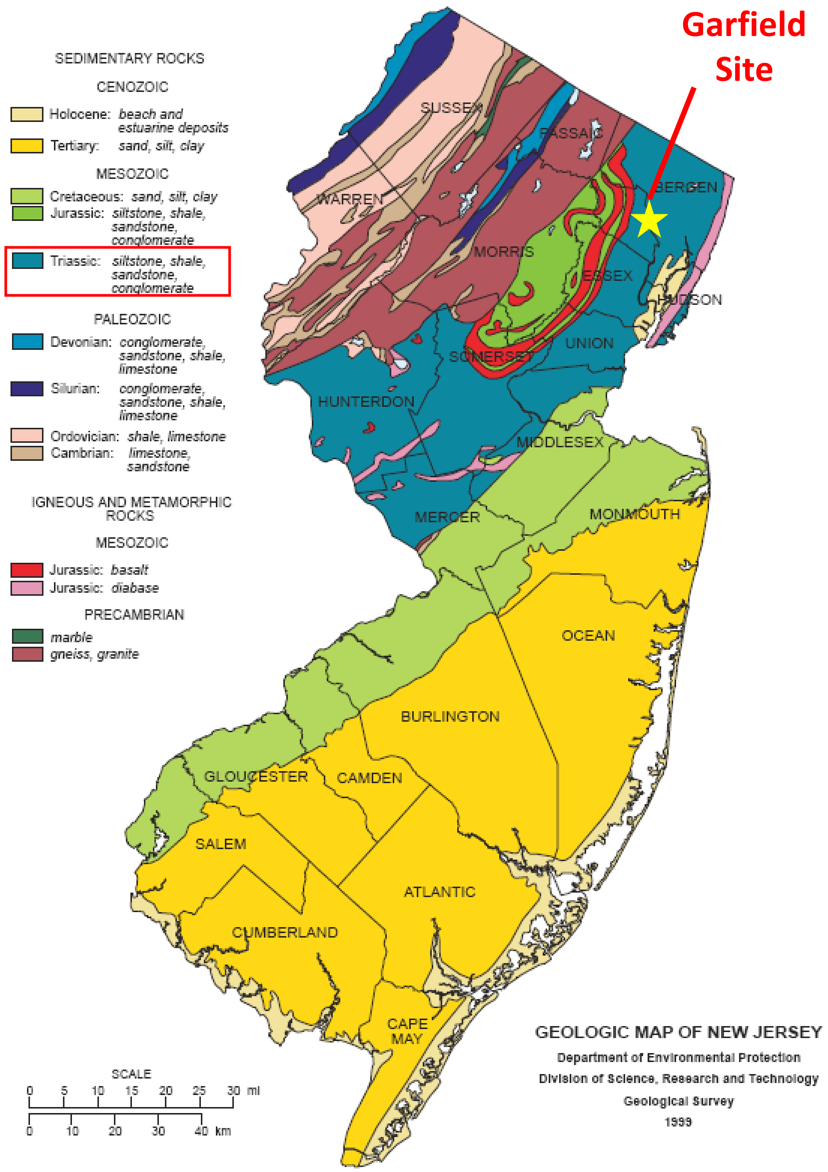
- Former electroplating facility
  - Operated from 1930's-2009
- 1983: chromic acid release (~3600 gal) from ruptured tank
  - 1984: on-site recovery well (~29% recovered)
- 1993: Cr contaminated groundwater and precipitate discovered in basement of downgradient fire station
- 2009: Extensive investigations initiated by EPA and sub-contractors
  - soil and groundwater sampling
  - health studies / basement sampling
  - on- and off-site remedial activities
- 2011-present: Extensive plume delineation
  - Monitoring well network incl. multilevel wells
- **2012-present: Matrix diffusion/reaction study**
  - ***coordinated with plume delineation***
  - ***focus of this talk***

Location


Garfield Cr Site
Garfield Chromium Superfund Site - Source
CDE Superfund Site
Park Ave Wellfield
NAWC Site
Pennsylvania Turnpike
Garden State Pkwy
Saw Mill Pkwy
Ocean Pkwy
Data SIO, NOAA, U.S. Navy, NGA, GEBCO
© 2012 Google
Image © 2012 TerraMetrics
35 km
lat 40.499236° lon -74.278086° elev 1 m
Eye alt 150.94 km
Google earth

NEW JERSEY GEOLOGY

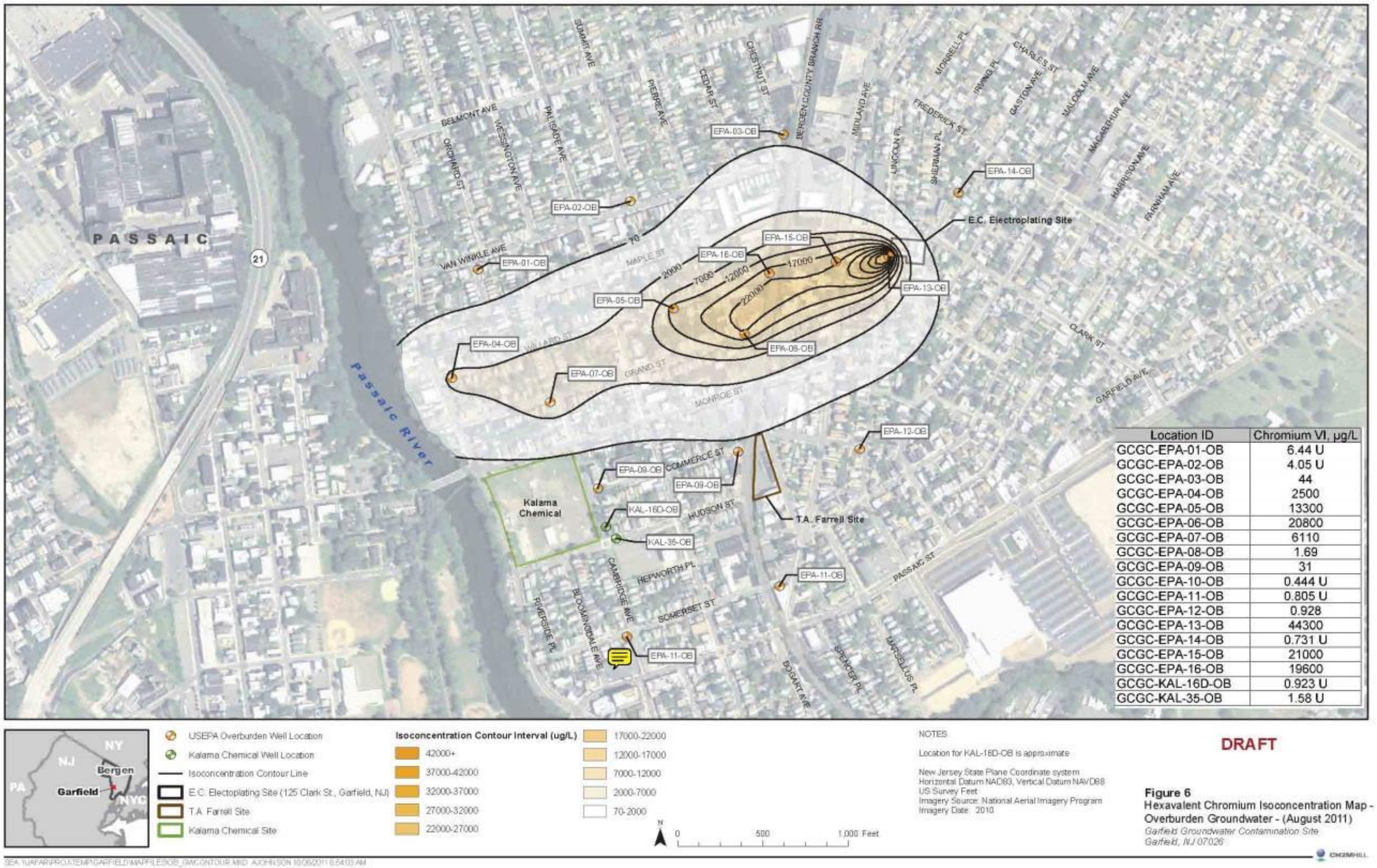
- Passaic (Brunswick Formation)
  - reddish-brown shale, siltstone and mudstone with a few green and brown shale interbeds
  - red and dark-gray interbedded argillites near the base
  - conglomerate and sandstone beds within the formation



http://www.state.nj.us/dep/njgs/enviroed/freedwn/psnjmap.pdf

Borehole Location

Cr(VI) Plume: Overburden



Location ID	Chromium VI, μg/L
GCGC-EPA-01-OB	6.44 U
GCGC-EPA-02-OB	4.05 U
GCGC-EPA-03-OB	44
GCGC-EPA-04-OB	2500
GCGC-EPA-05-OB	13300
GCGC-EPA-06-OB	20800
GCGC-EPA-07-OB	6110
GCGC-EPA-08-OB	1.69
GCGC-EPA-09-OB	31
GCGC-EPA-10-OB	0.444 U
GCGC-EPA-11-OB	0.805 U
GCGC-EPA-12-OB	0.928
GCGC-EPA-13-OB	44300
GCGC-EPA-14-OB	0.731 U
GCGC-EPA-15-OB	21000
GCGC-EPA-16-OB	19600
GCGC-KAL-16D-OB	0.923 U
GCGC-KAL-35-OB	1.58 U

Figure from EPA / CH2M Hill

CR(VI) PLUME: BEDROCK

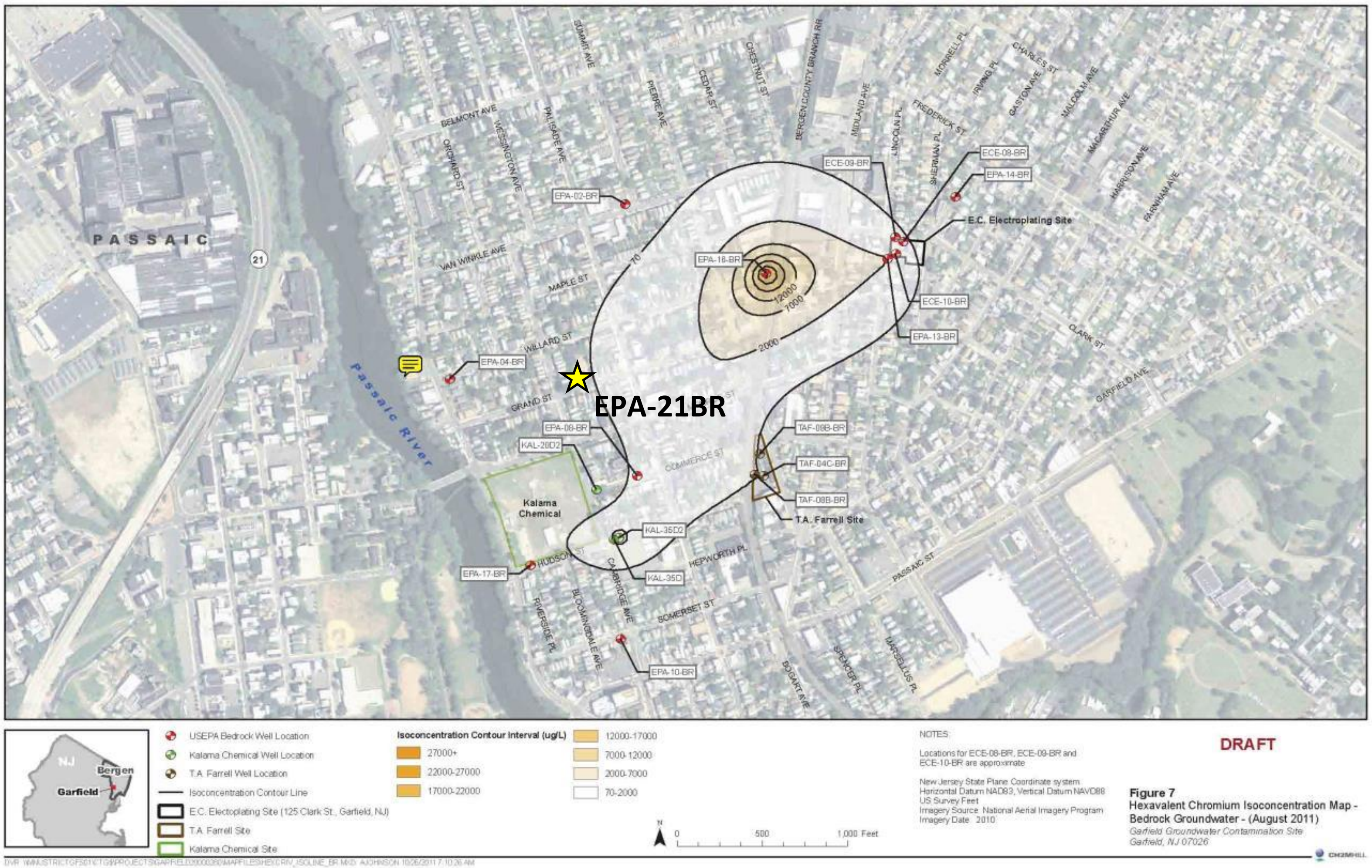
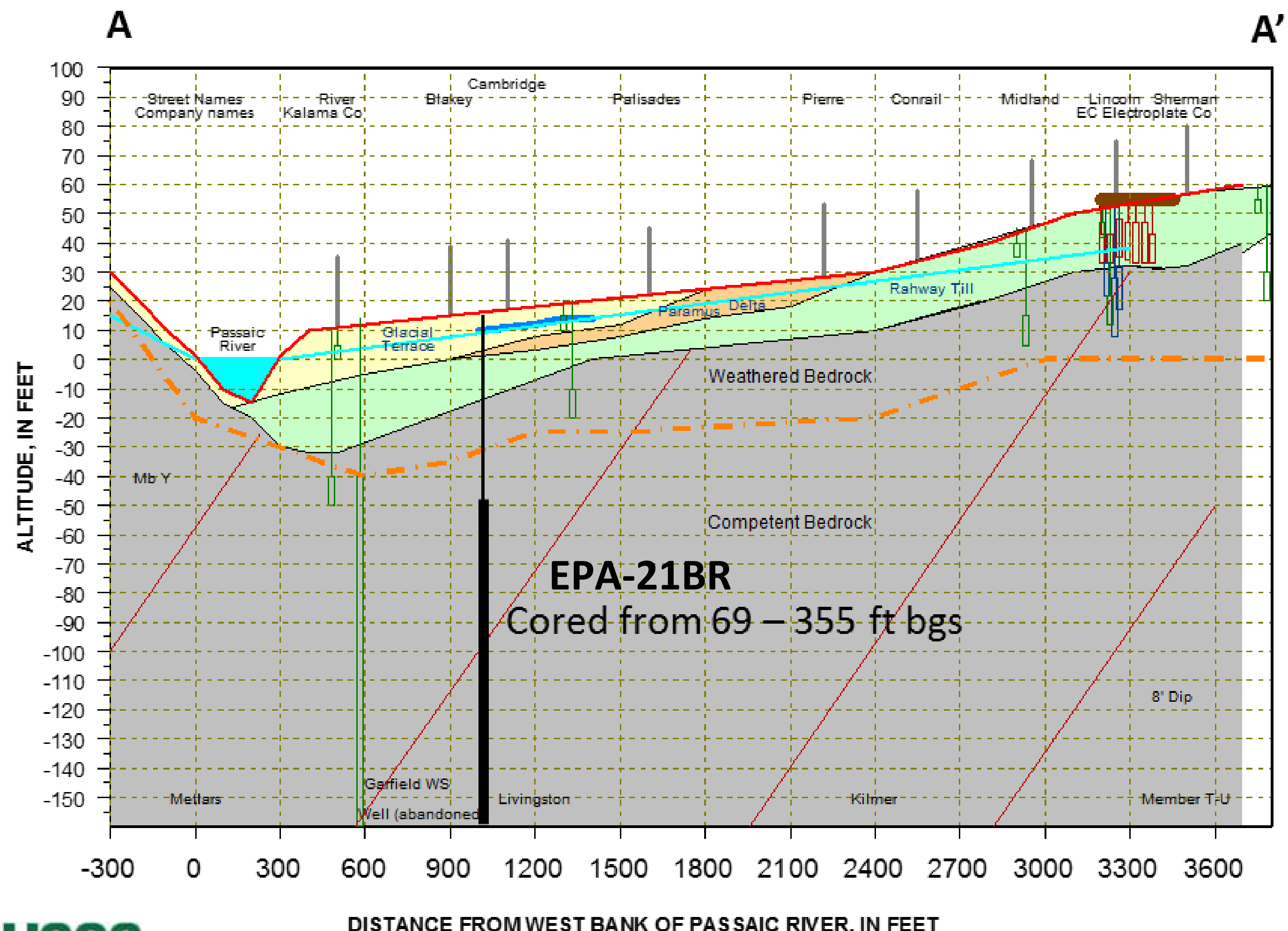


Figure from EPA / CH2M Hill

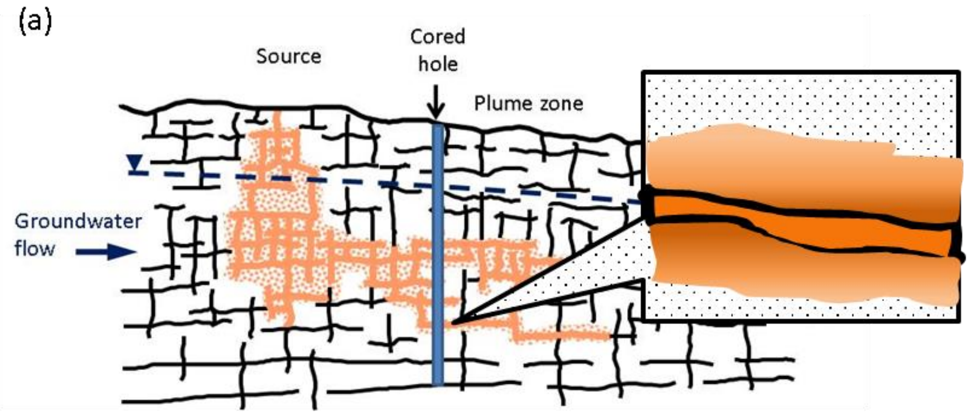
Vertical Cross-Section

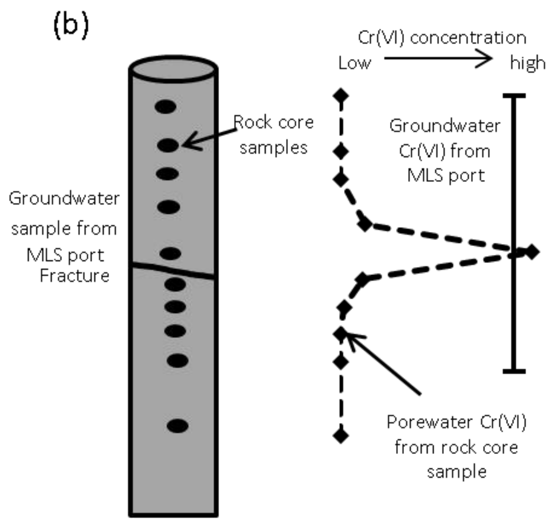


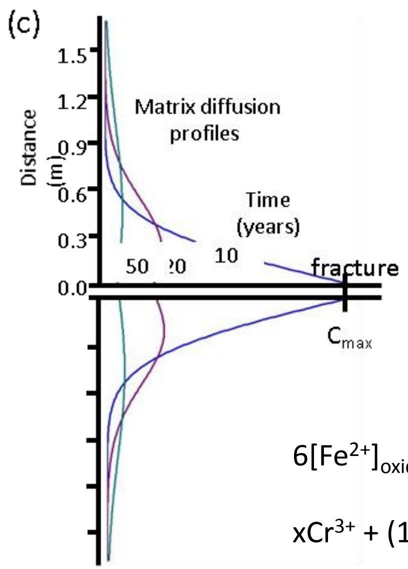
USGS science for a changing world

Slide from P. Lacombe, USGS

Conceptual Model







Long-term decline due to back diffusion and in-situ reduction

- How significant is reduction?

$$6[Fe^{2+}]_{oxide} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6[Fe^{3+}]_{oxide} + 2Cr^{3+} + 7H_2O$$

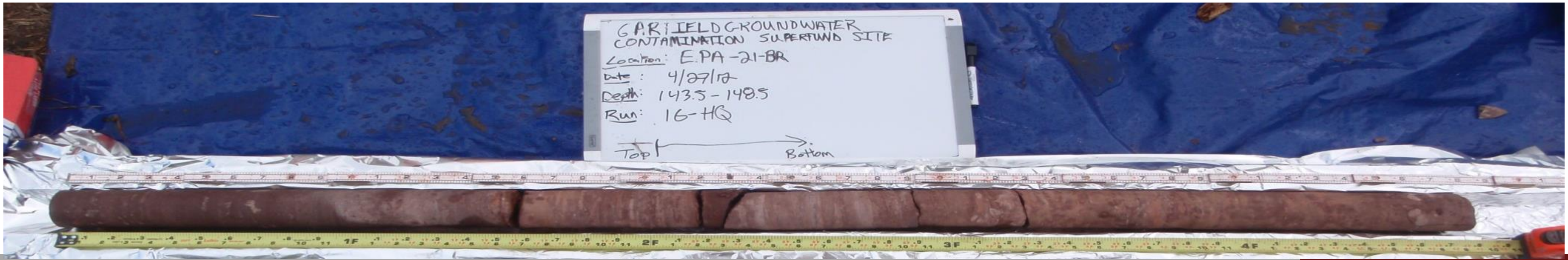
$$xCr^{3+} + (1-x)Fe^{3+} + 3H_2O \rightarrow (Cr_xFe_{1-x})(OH)_3(s) + 3H^+$$

Objectives

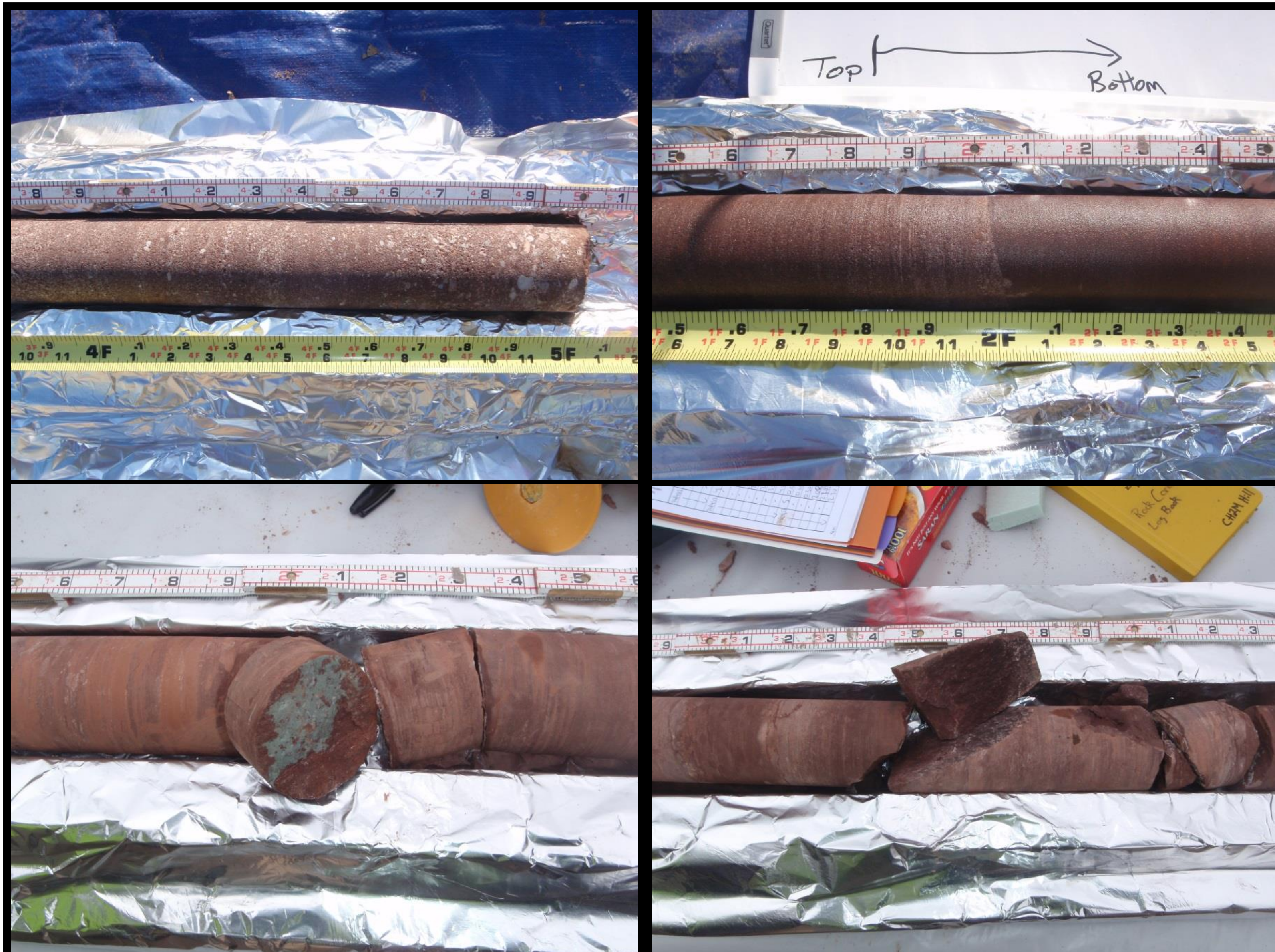
- Phase I:
  - Develop extraction method for Cr(VI) in porewater
  - Detailed profile of Cr(VI) concentrations
  - Compare with groundwater Cr(VI) distribution from multilevel well
- Phase II:
  - Develop extraction method for Cr(III) – product of Cr(VI) reduction
  - Detailed profile of Cr(III) in bedrock
  - Mass balance for Cr(VI) and Cr(III) to assess extent of natural attenuation

Rock Core Collection

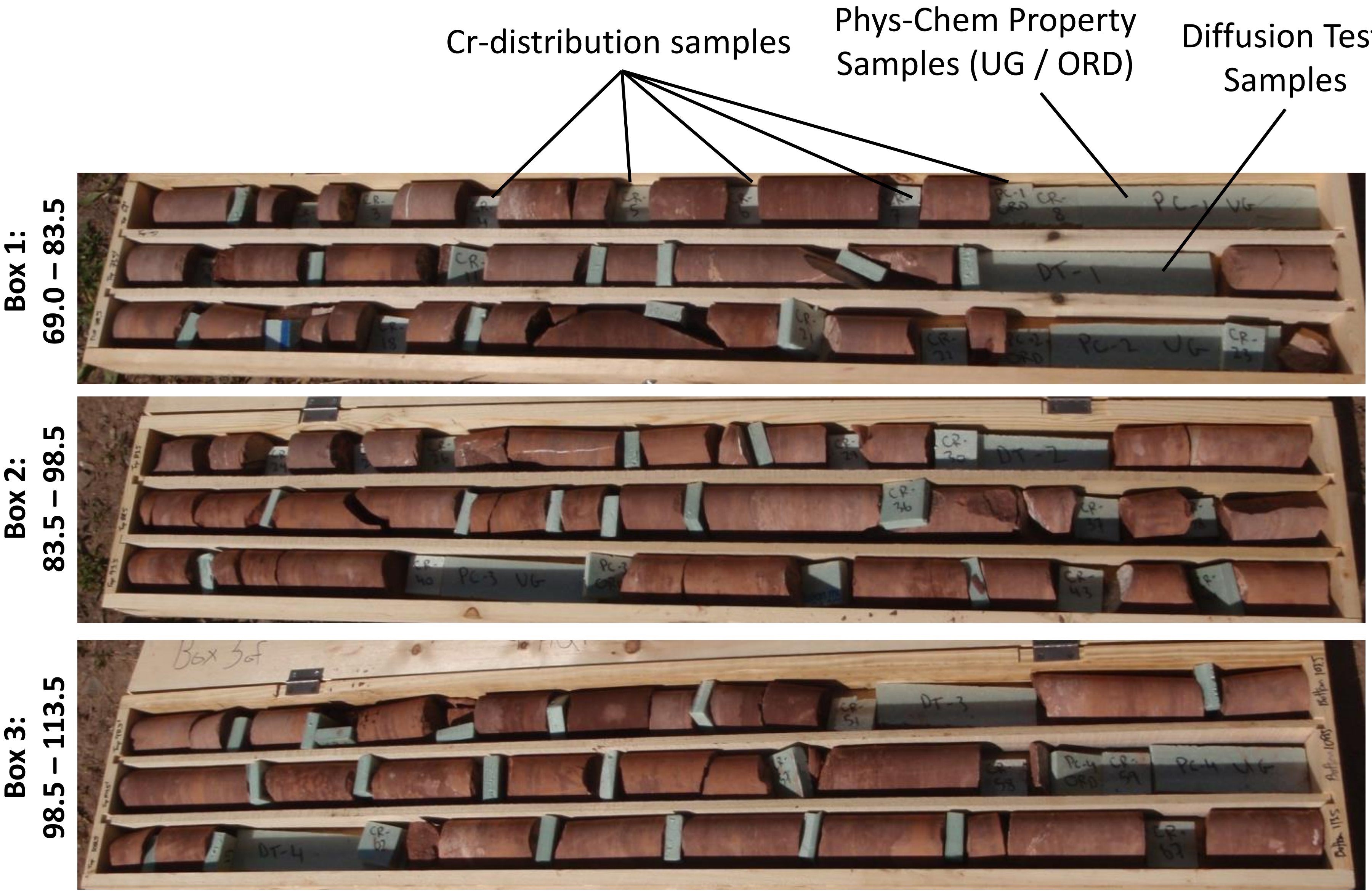
Triple-tube core barrel



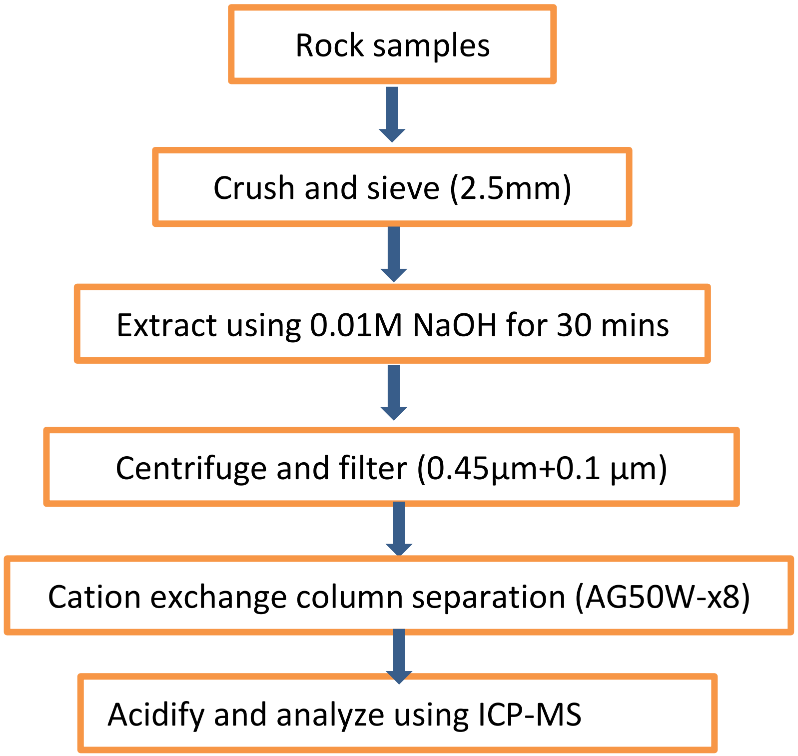
Rock Core Subsampling



Rock Core Subsampling

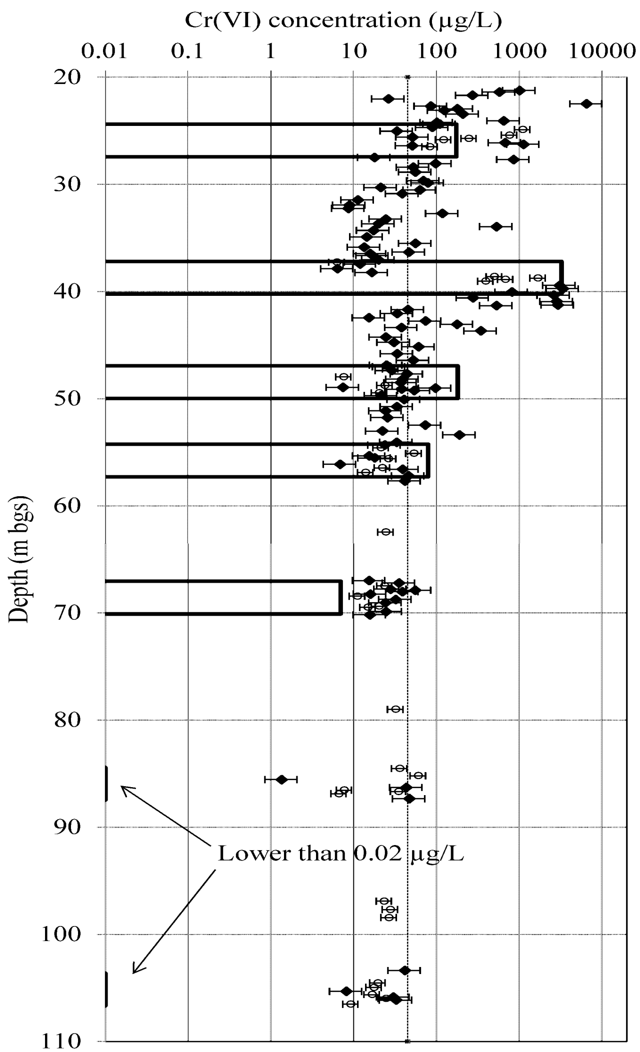


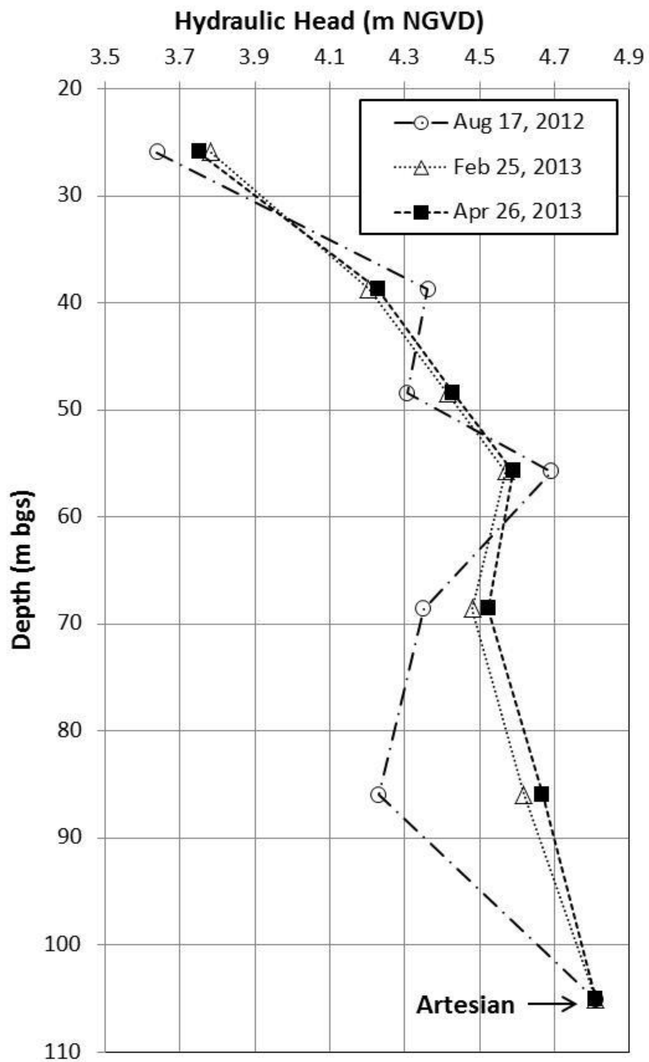
Phase I: NaOH Extraction - Cr(VI)



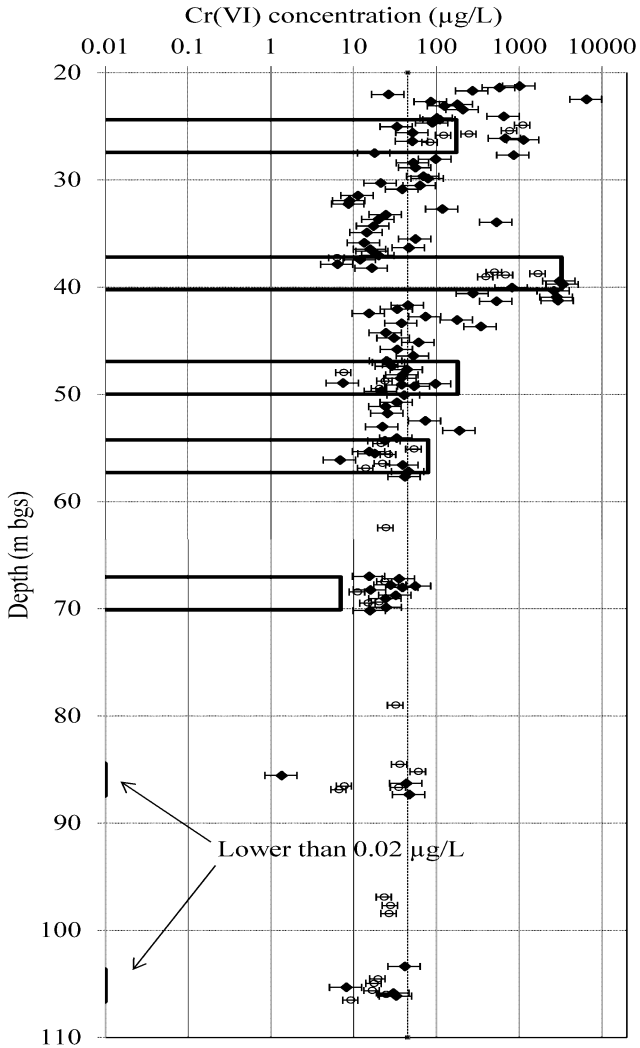
- Sample was crushed and sieved (<2.5mm)
- 1.5 g sample in 10 mL 0.01 mol/L NaOH
- Placed on rotator and extracted for 30 minutes
- Centrifuged and filtered (< 0.45 µm & 0.1 µm), washed with 5 mL of 0.01 mol/L NaOH, then acidified with nitric acid to pH 2-5
- Ion exchange column: 1 mL AG50W-x8 cation-exchange resin
- Elute with 10 mL 0.01% HNO_3
- Acidify eluent to 1% HNO_3
- ICP-MS analysis

Cr(VI) vs Depth





Cr(VI) vs Depth

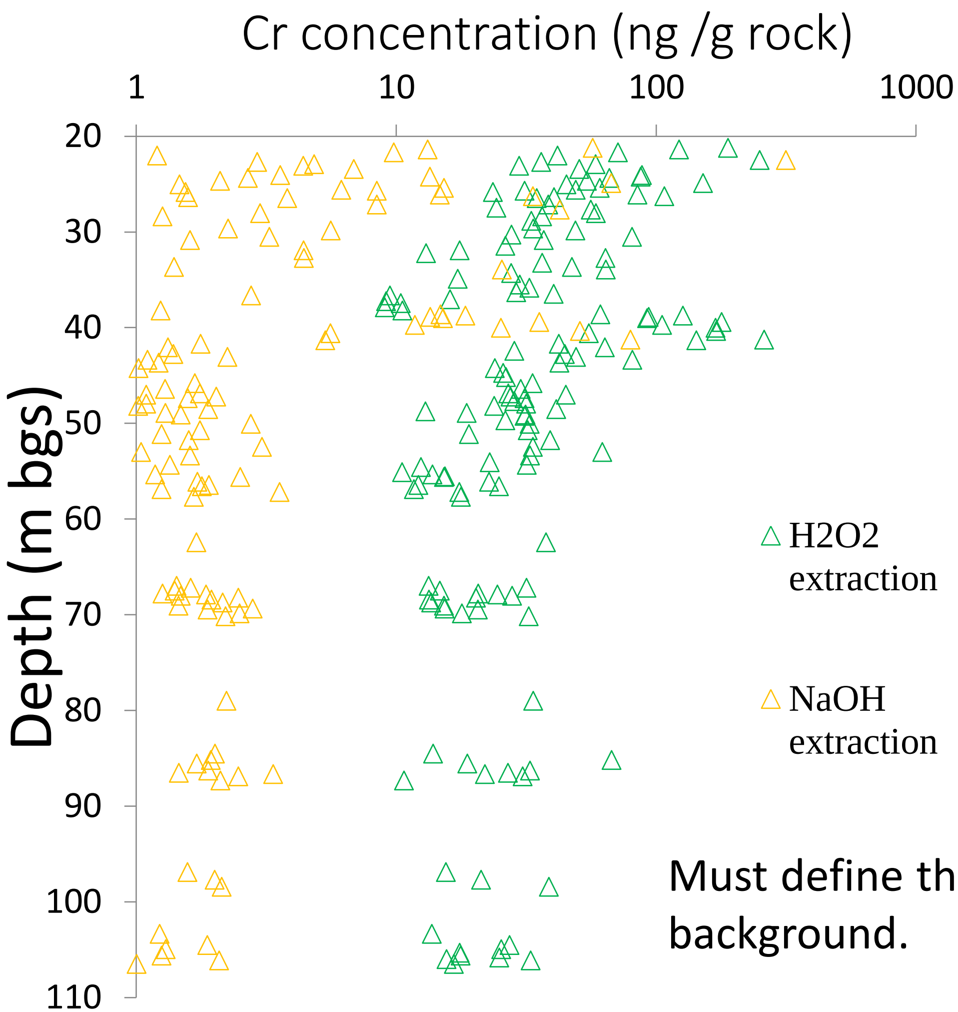


- Detailed core sampling provides clear picture of Cr(VI) concentrations and mass distribution
- No information on the extent of natural attenuation
  - this requires information on Cr(III) distribution

Phase II: H_2O_2 Extraction

- H_2O_2 extraction (Cr(VI) and labile Cr(III)):
  - About 1g rock sample (< 2mm)
  - Extractant: 5% H_2O_2 in 0.1M ammonium acetate (pH 7)
  - Extraction time: 30 minutes
  - Three sequential extraction (10 mL x 3)
- NaOH extraction (Cr(VI)):
  - About 1g rock sample (< 2mm)
  - Extractant: 0.01 M NaOH 10 mL
  - Extraction time: 30 minutes
  - Another 5 mL of 0.01M NaOH to completely extract Cr(VI)
  - Cation exchange separation
- ICP-MS analysis
- Labile Cr(III): the difference between H_2O_2 and NaOH extraction

Extraction Data



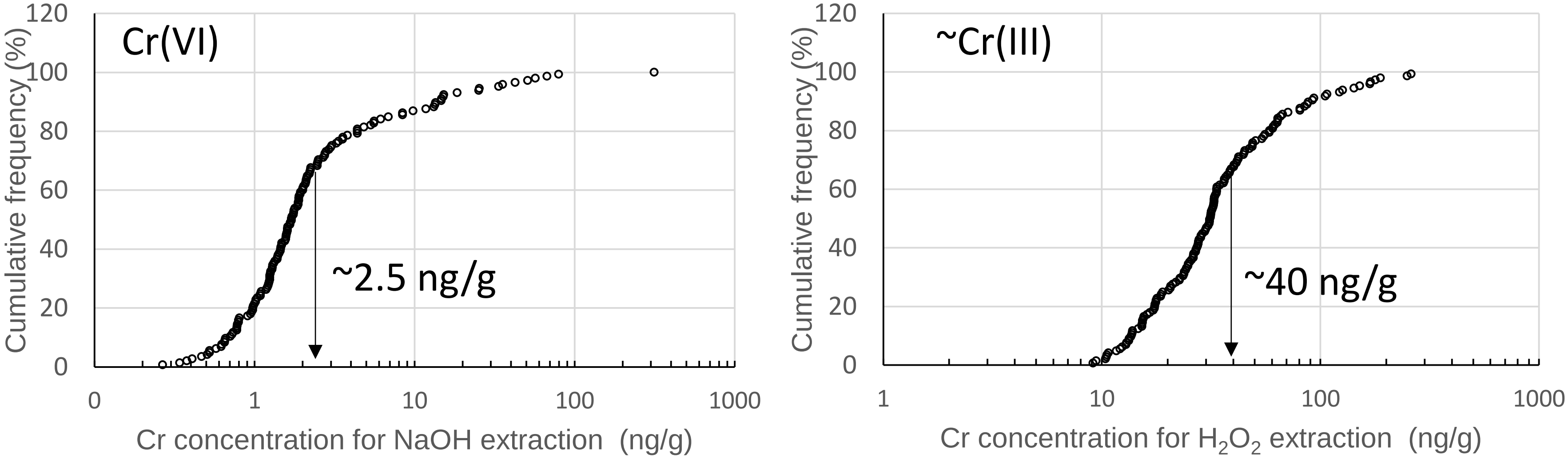
Must define threshold for natural Cr(III) background.

NATURAL CR BACKGROUND

Natural Cr background and extractable Cr concentrations for uncontaminated rocks and aquifer sands (mean ±1SD). LRS is lab made reference samples from uncontaminated zones.

		Extractable Cr (mg/g rock)	
	Total Cr (µg /g rock)	H_2O_2 Extraction (n=3)	NaOH Extraction (n=3)
LRS	55.0±1.9 (n=3)	0.040±0.004	0.0010±0.0006
Meta gabbro	26.7±1.9 (n=2)	0.017±0.004	0.0012±0.0004
Granitic gneiss	5.3±0.1 (n=2)	0.008±0.002	0.0010±0.0006
Sand stone (unoxidized)	5.3±0.1 (n=2)	0.018±0.002	0.0019±0.0001
Sand stone (oxidized)	38.8±1.0 (n=2)	0.030±0.005	0.0015±0.0004
Sand (NB)	28.7±6.8 (n=2)	0.034±0.001	0.0017±0.0005
Sand (SK)	17.5±0.3 (n=2)	0.060±0.005	0.0016±0.0003
Mean	25.3	0.030	0.0014
Chromite	249,000	0.500±0.017	0.012±0.001

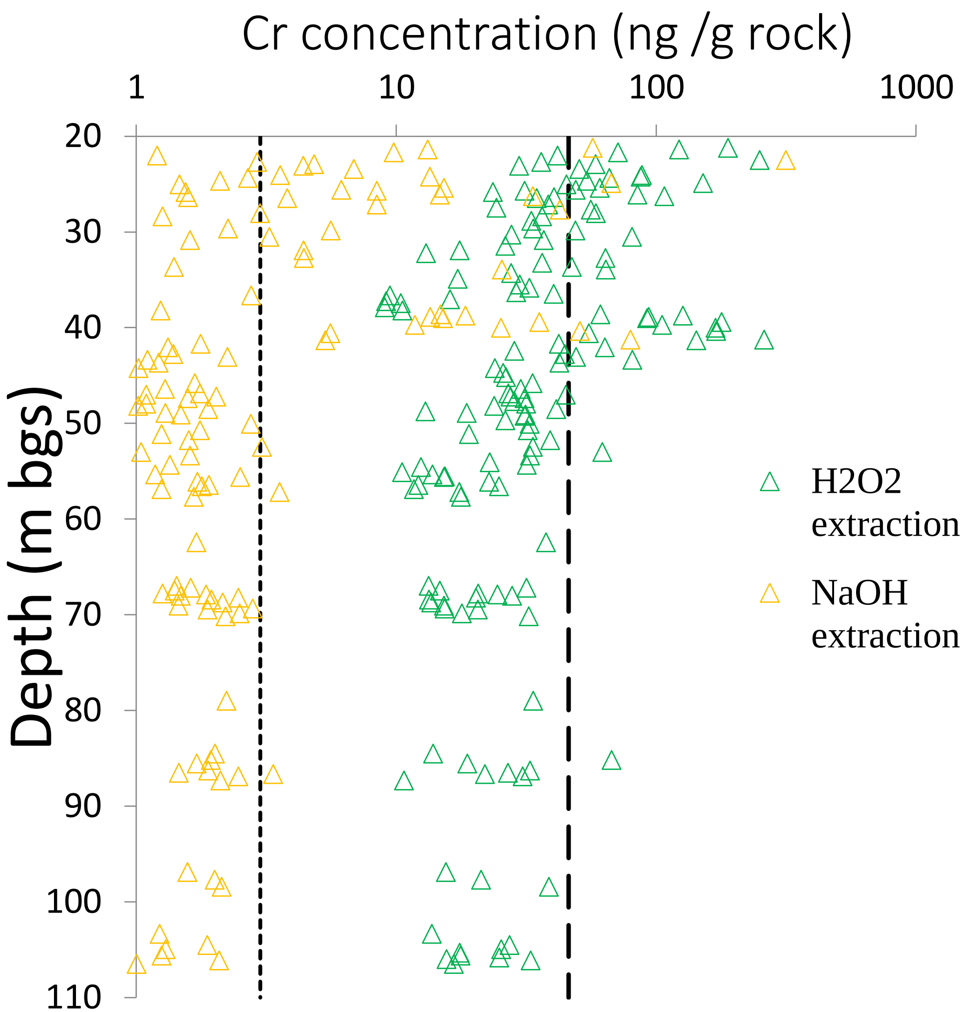
Garfield Site: Background and Threshold



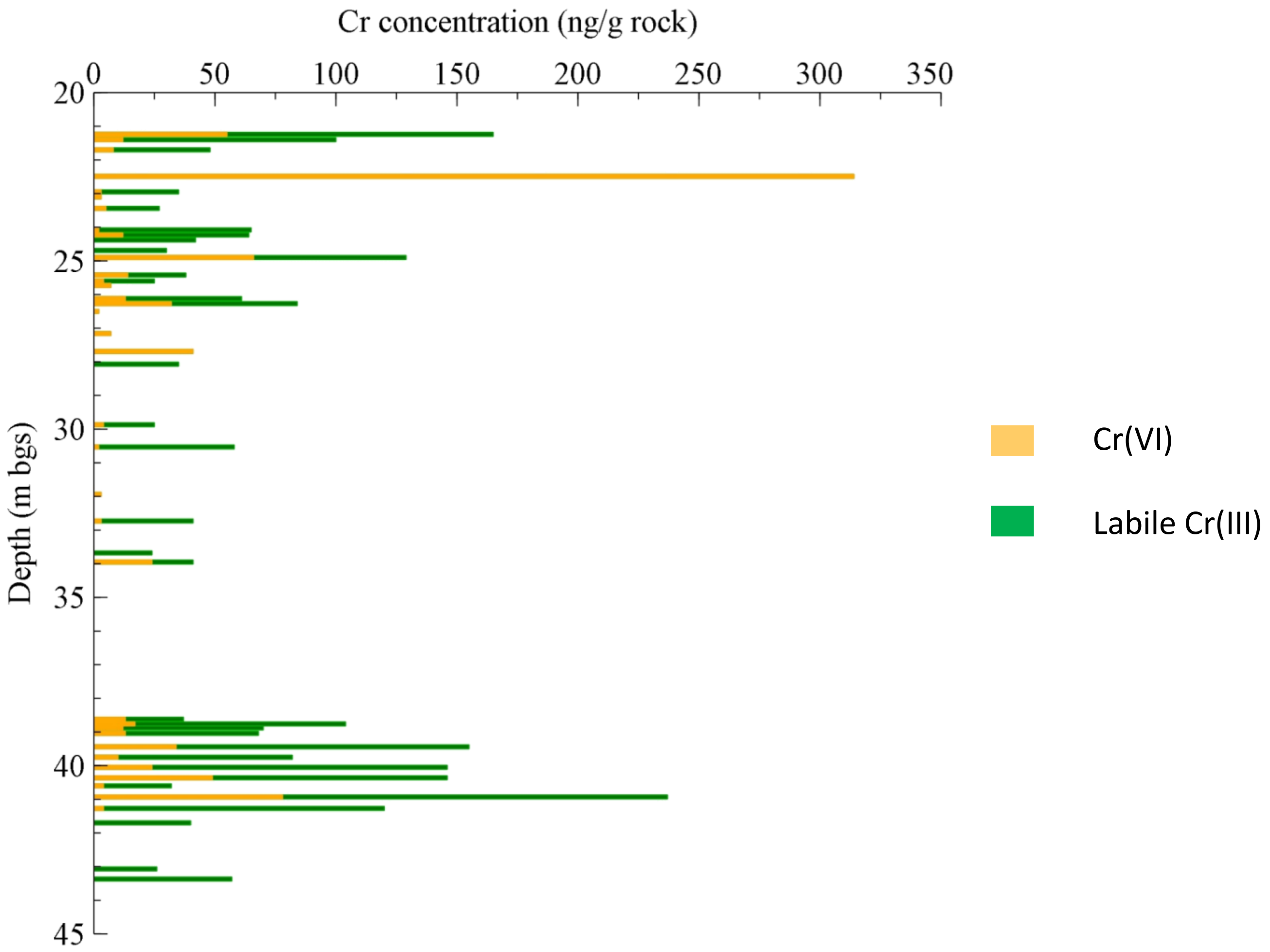
Garfield Site: Background and Threshold

	H_2O_2 extraction (ng/g)		NaOH extraction (ng/g)	
	Mean	SD	Mean	SD
<50 m bgs (n=56)	23.8	10.8	1.7	0.7
<60 m bgs (n=36)	23.4	10.8	1.8	0.6
<80 m bgs (n=20)	24.5	12.6	1.7	0.6
Threshold	~45 ng/g		~3.1 ng/g	

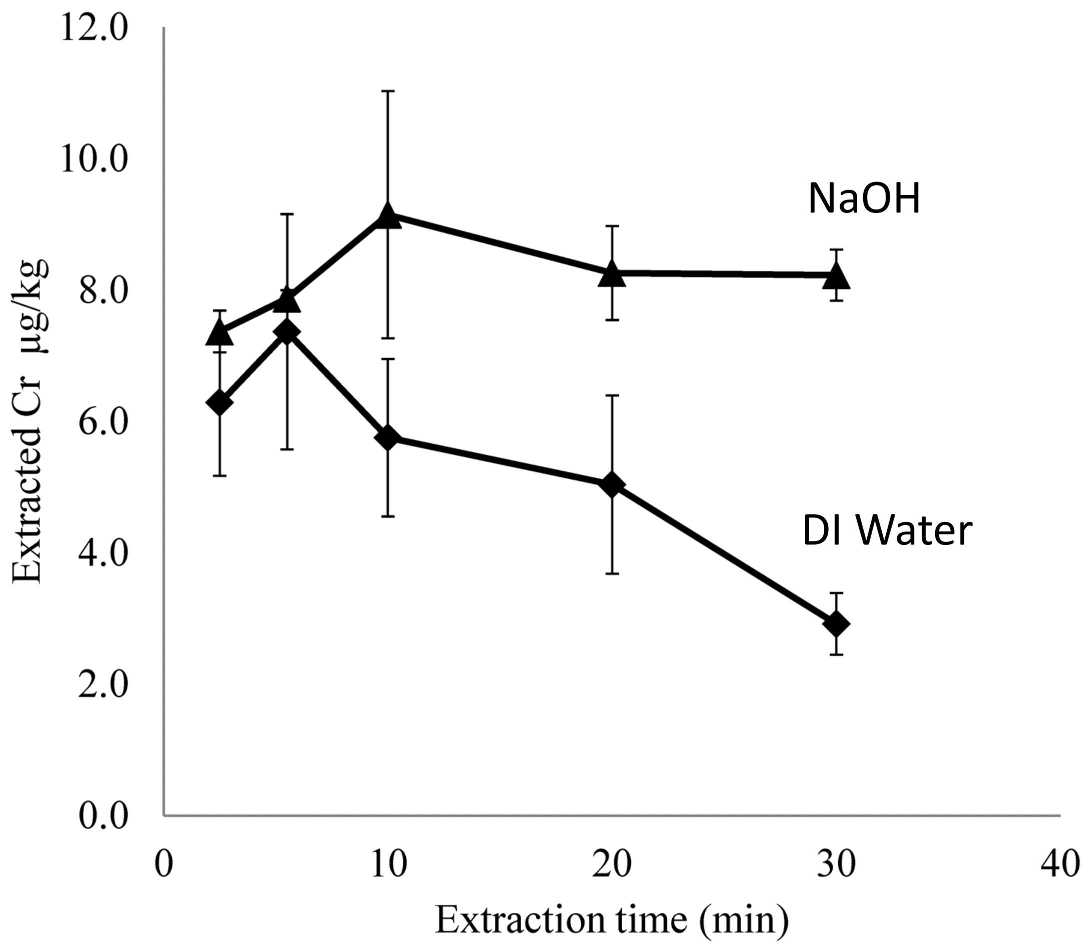
Extraction Data with Thresholds



Mass Balance: Cr(VI) and labile Cr(III)

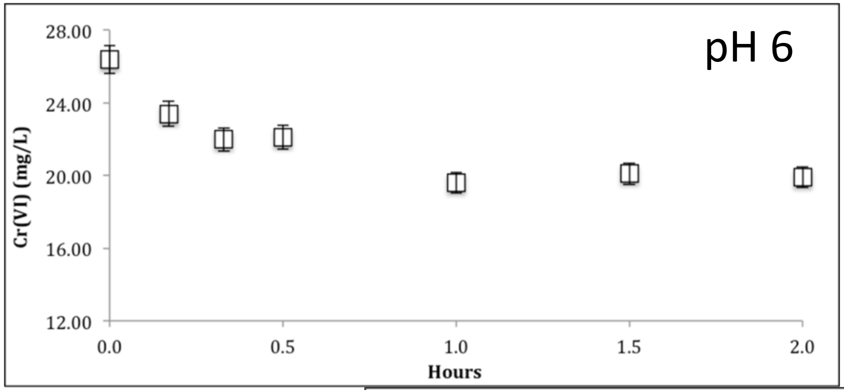


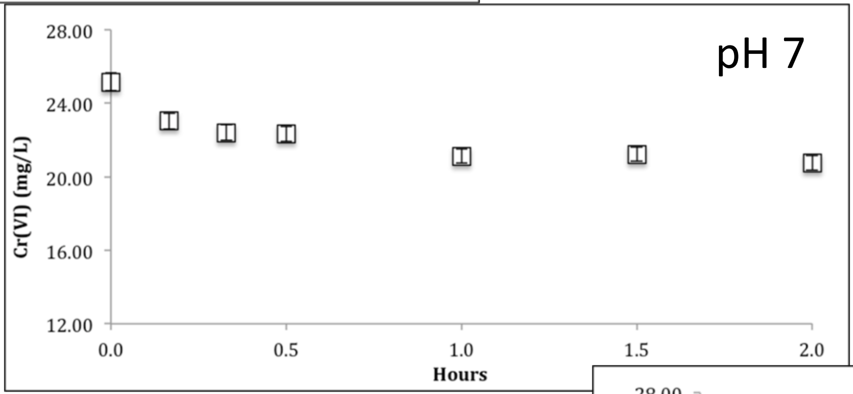
Reaction Processes

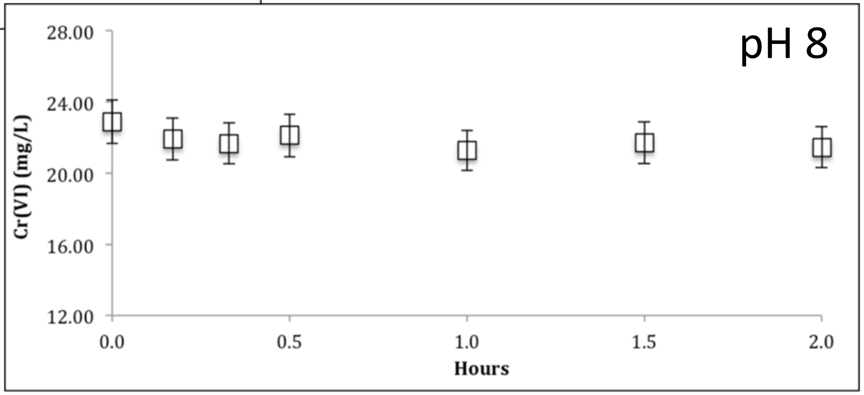


Reaction Processes

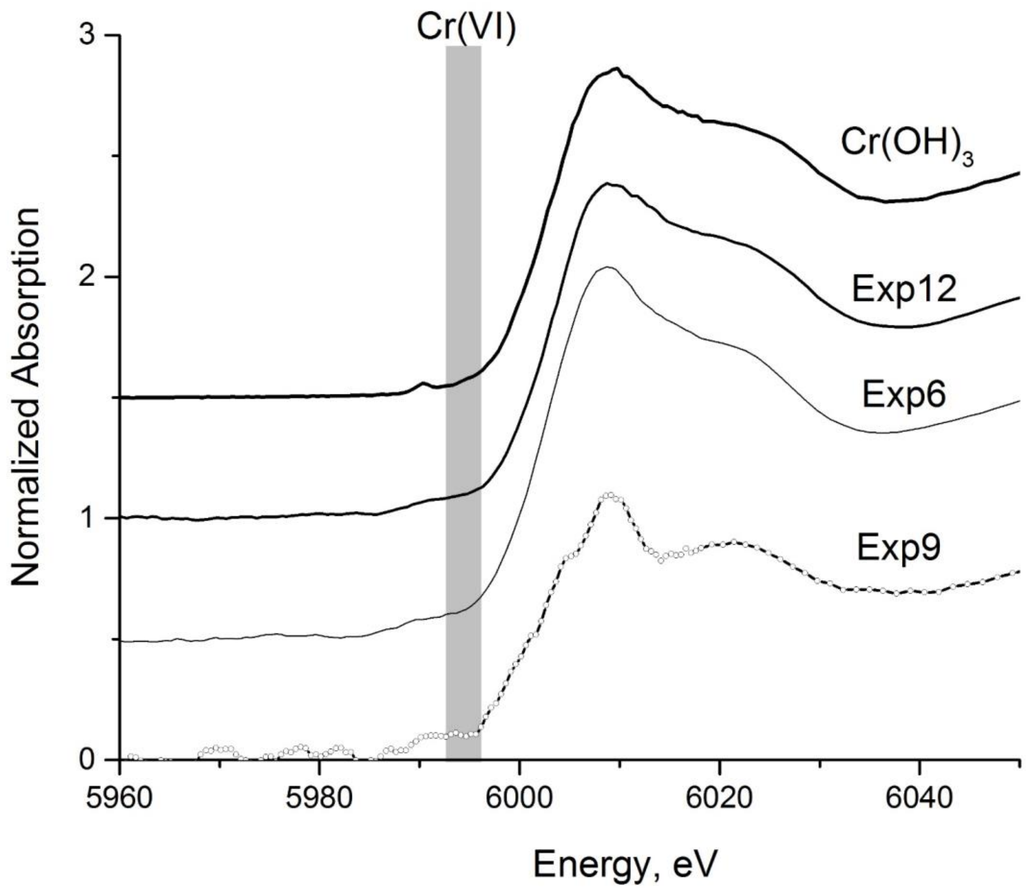
Reaction of Cr(VI) on the surface of chlorite







Reaction Products: XANES



SUMMARY

- High density Cr(VI) data clearly defines the contaminant distribution
- Additional focus on the solid-phase Cr(III) reaction product demonstrates conclusively that natural attenuation is underway - in a red bed sequence!
- Mass distribution is about 50:50 Cr(III):Cr(VI)
- Mineralogical work is underway to define the reactive mineral phases

THANKS FOR YOUR ATTENTION

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