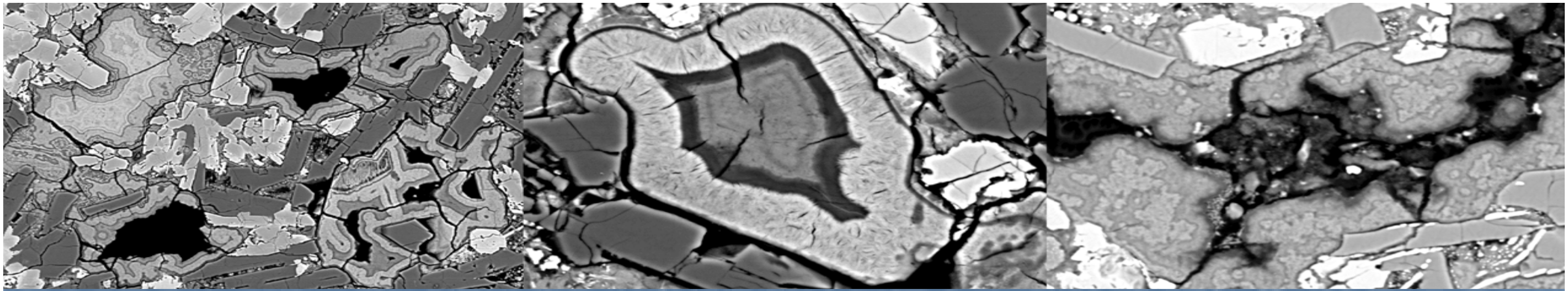
PNNL-SA-60570



Geochemical Studies with Hanford 300-Area Sediments

IFC Meeting April 29-30, 2008

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USGS science for a changing world

Office of Science U.S. DEPARTMENT OF ENERGY

JOHNS HOPKINS UNIVERSITY

Site Description

300 AREA - North and South Processing Ponds

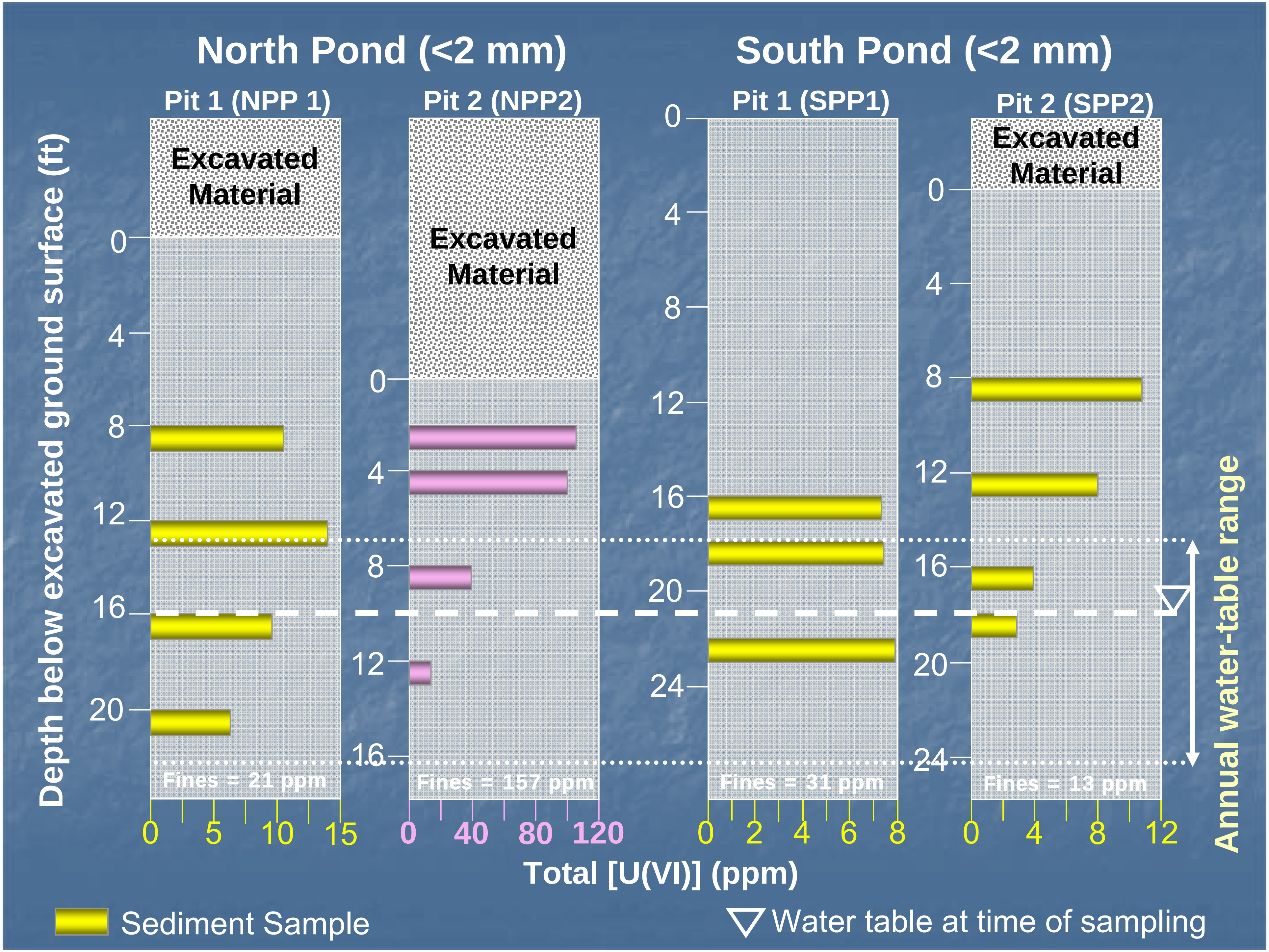
1943-1975	1996 / 2001	2003	2004
Liquid disposal units	>640,000 t contaminated soil removed	4 pits excavated to ∇	Backfilled with inert material

South Pit 1

South Pit 2

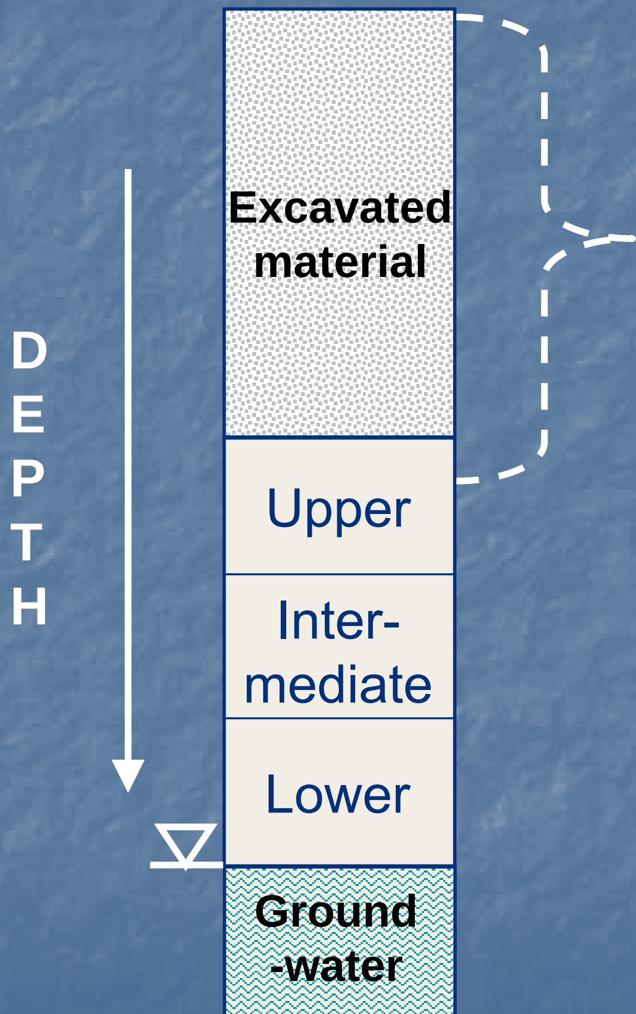
North Pit 2

North Pit 1

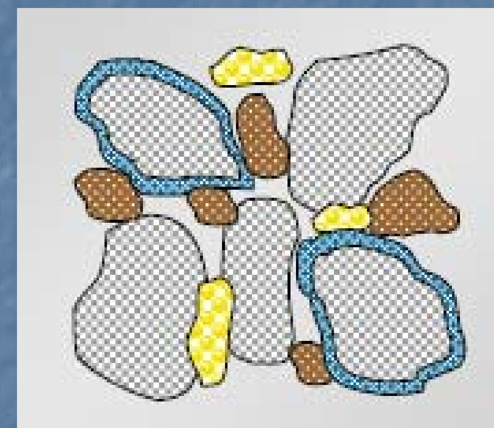


North Pond (<2 mm)
South Pond (<2 mm)
Pit 1 (NPP 1)
Pit 2 (NPP2)
Pit 1 (SPP1)
Pit 2 (SPP2)
Excavated Material
Excavated Material
Excavated Material
Depth below excavated ground surface (ft)
0
4
8
12
16
20
24
Fines = 21 ppm
Fines = 157 ppm
Fines = 31 ppm
Fines = 13 ppm
0 5 10 15
0 40 80 120
0 2 4 6 8
0 4 8 12
Total [U(VI)] (ppm)
Annual water-table range
Sediment Sample
Water table at time of sampling

U(VI) Speciation in Vadose Zone Sediments

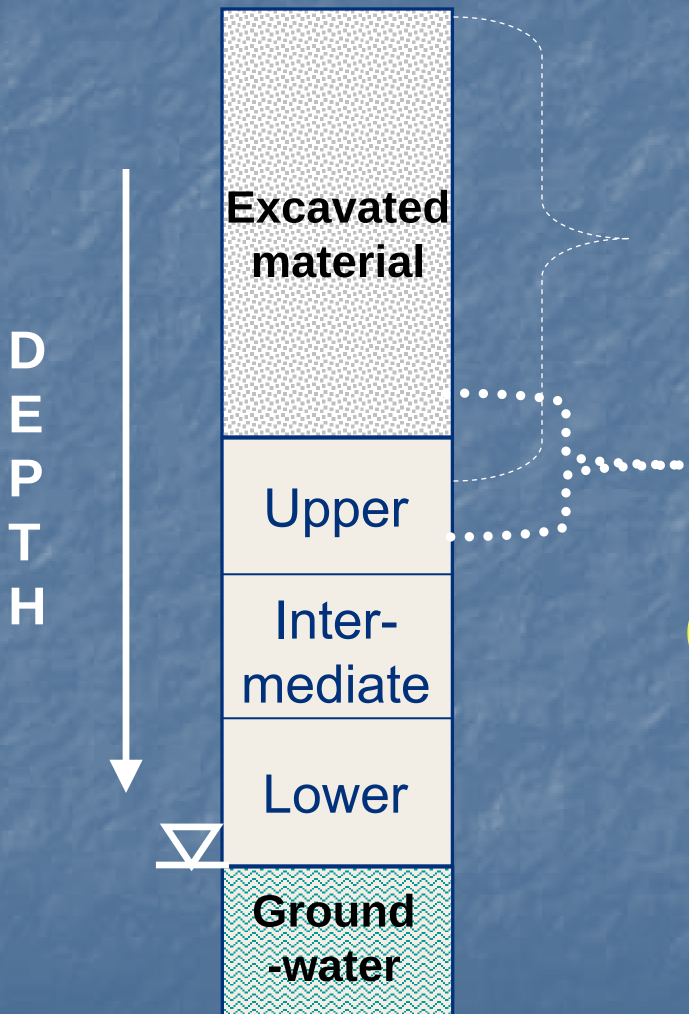


Dispersed U(VI) coprecipitated in calcite

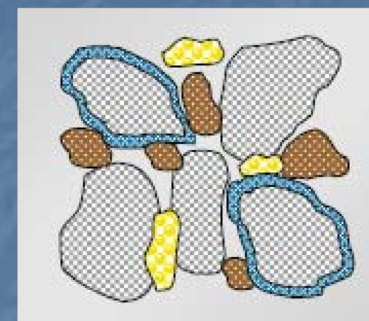


Wang et al, 2005

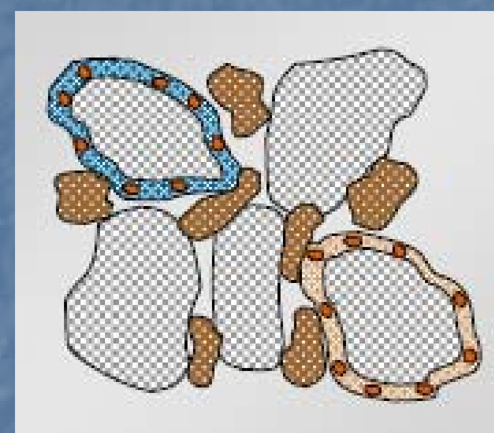
U(VI) Speciation in Vadose Zone Sediments



Dispersed U(VI) coprecipitated in calcite

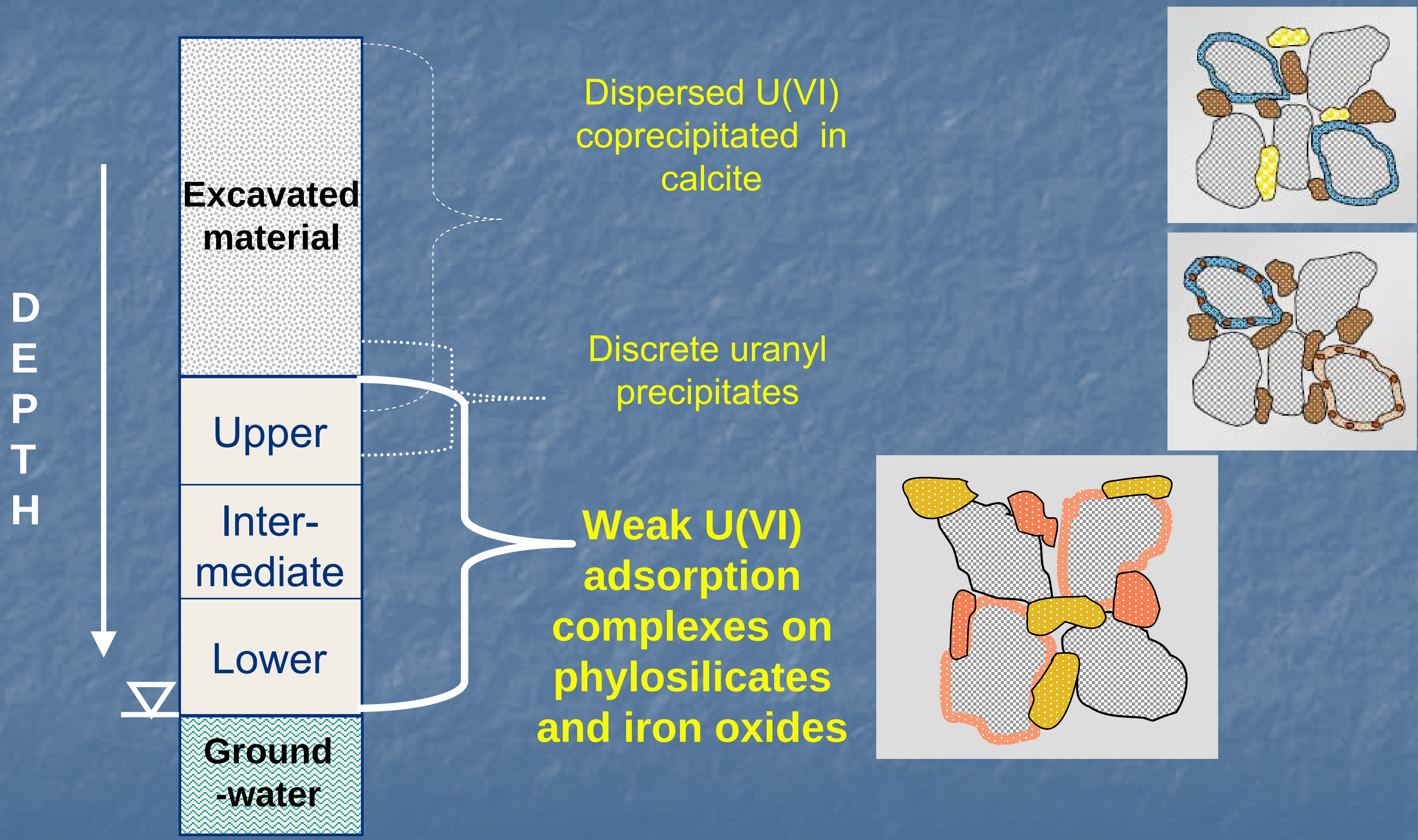


Discrete uranyl phosphate precipitates (metatorbernite)



Catalano et al, 2006; Arai et al, 2007

U(VI) Speciation in Vadose Zone Sediments



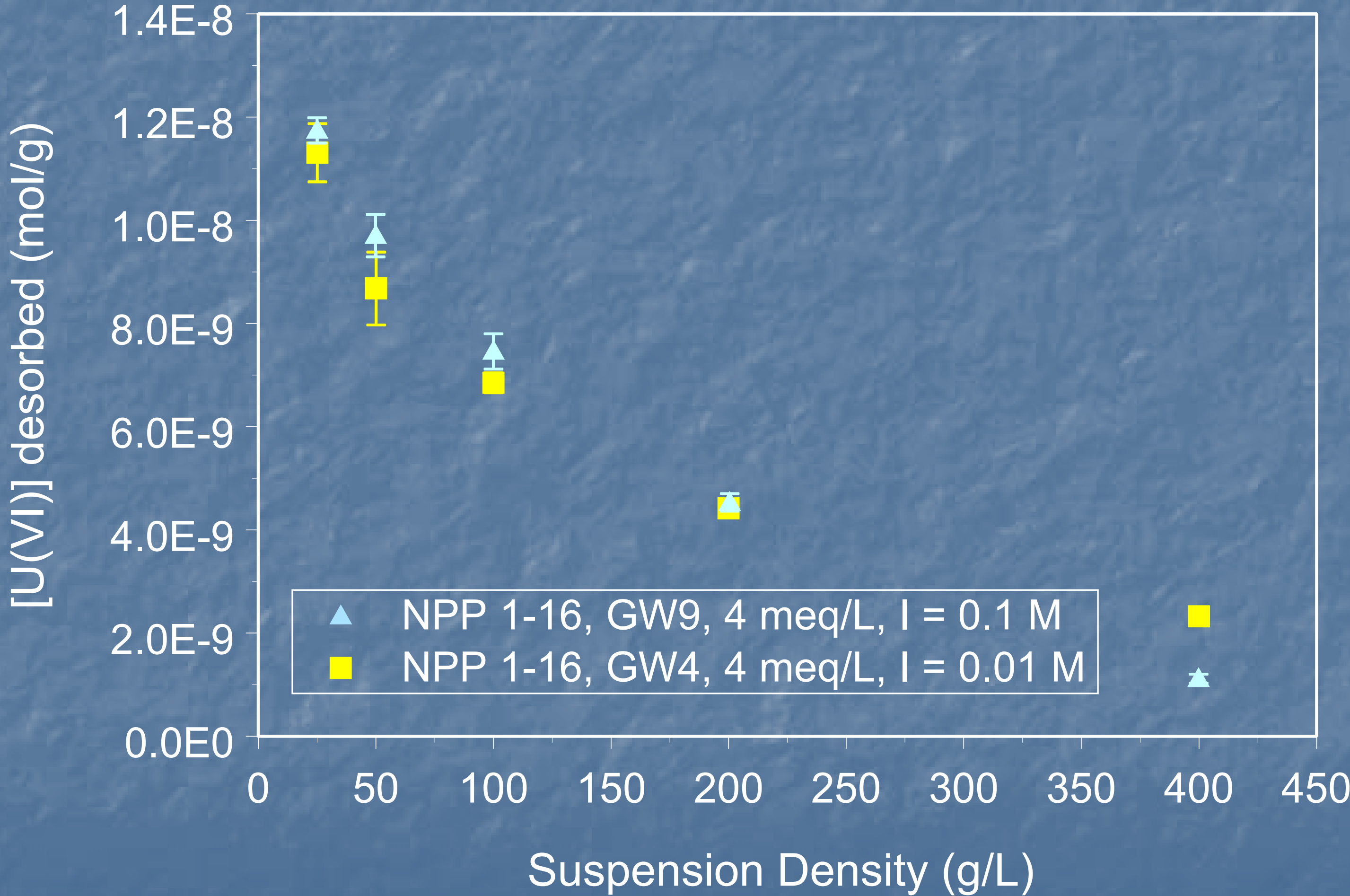
Catalano et al, 2006

Methods

- Sediment Characterization
  - BET hysteresis, S.A., γ-counting, Hg porosimetry, size-fraction analysis, combined with previous characterization[1]
- Artificial Groundwater (AGW) Desorption/Dissolution Kinetics and Sorption Isotherms
  - variable alkalinity, suspension density, and I, individual size fractions
- Surface Complexation Modeling
  - Non-electrostatic, generalized composite approach
- Isotopic Exchange Reactions
  - ^{233}U tracer spike after 24 or 1260 hr pre-equilibration
- Chemical Extractions
  - Sodium (bi)carbonate (pH ~9) & Dilute sodium formate (pH ~3.5),
- Column and Batch Porosity Investigation
  - ^{3}H and Br, long term storage, elution with stop-flow events
  - Modeling of diffusion

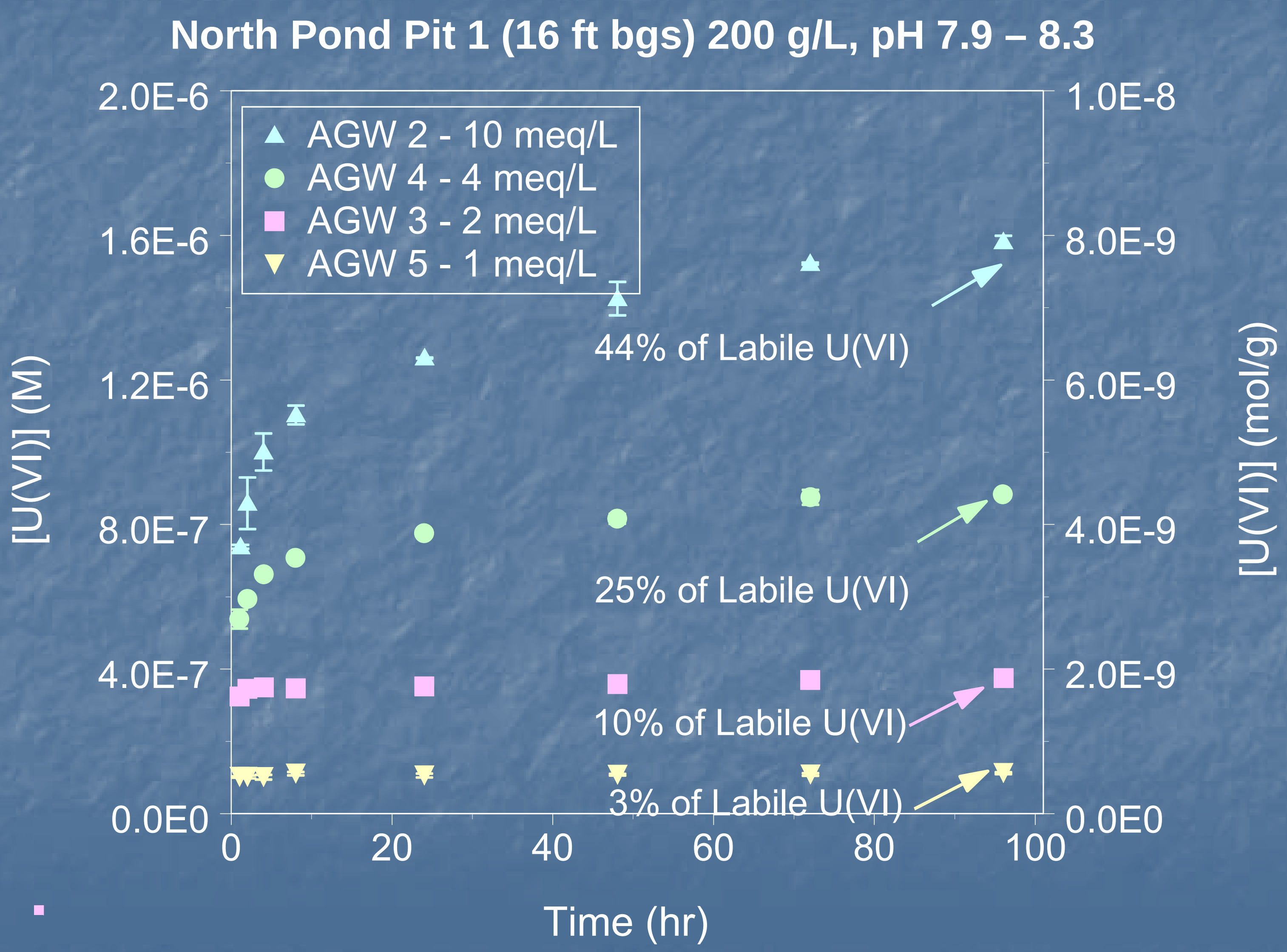
[1] Serne et al., 2003; Qafoku et al., 2005; Zachara et al., 2005; Catalano et al., 2006; Arai et al, 2007; Stubbs et al 2008

U(VI) Release from Hanford Sediments in Batch Reactions

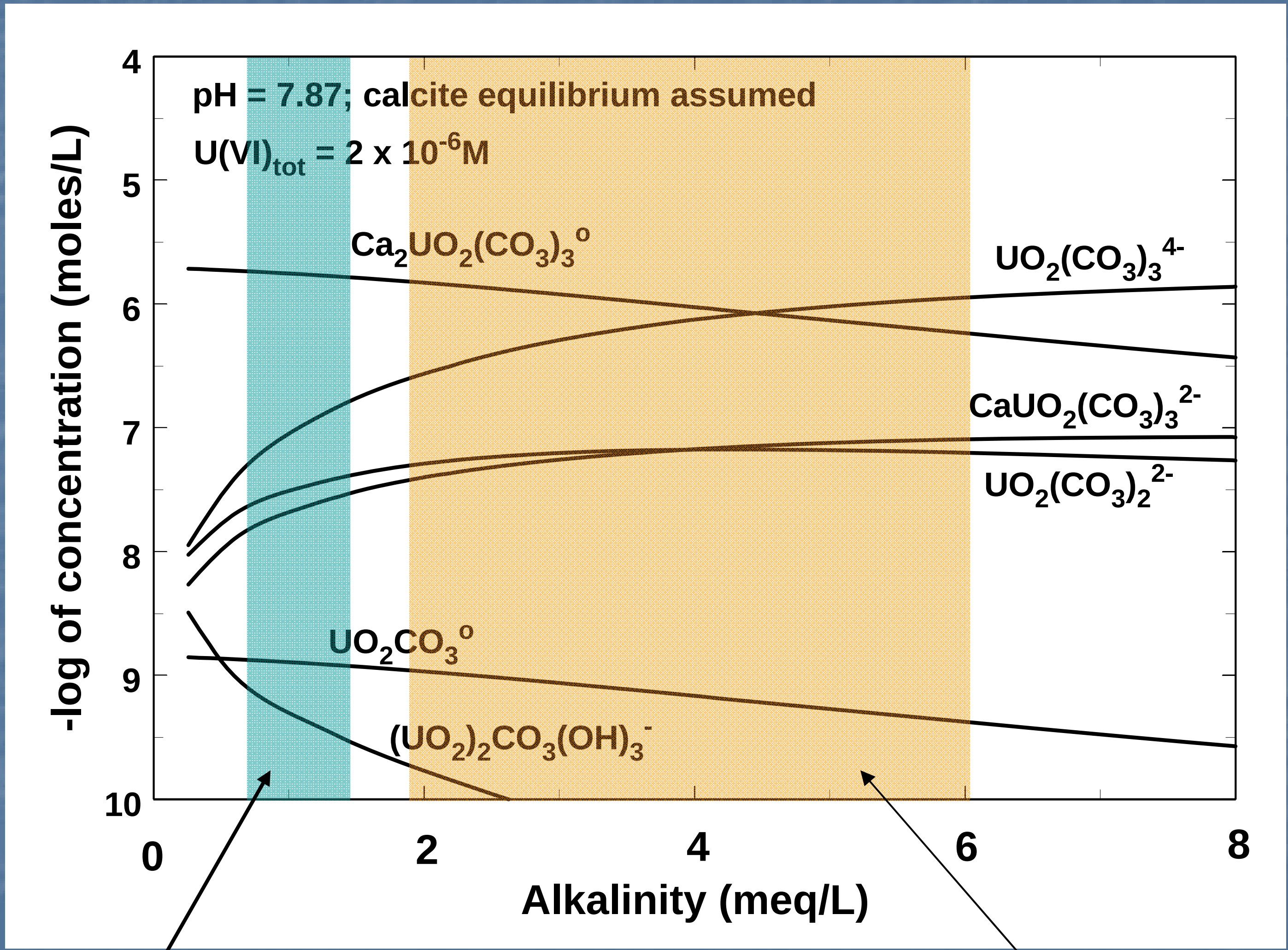


pH 7.9 – 8.3, Alkalinity = 4 meq/L, 72 hr

Alkalinity Effects on U Release



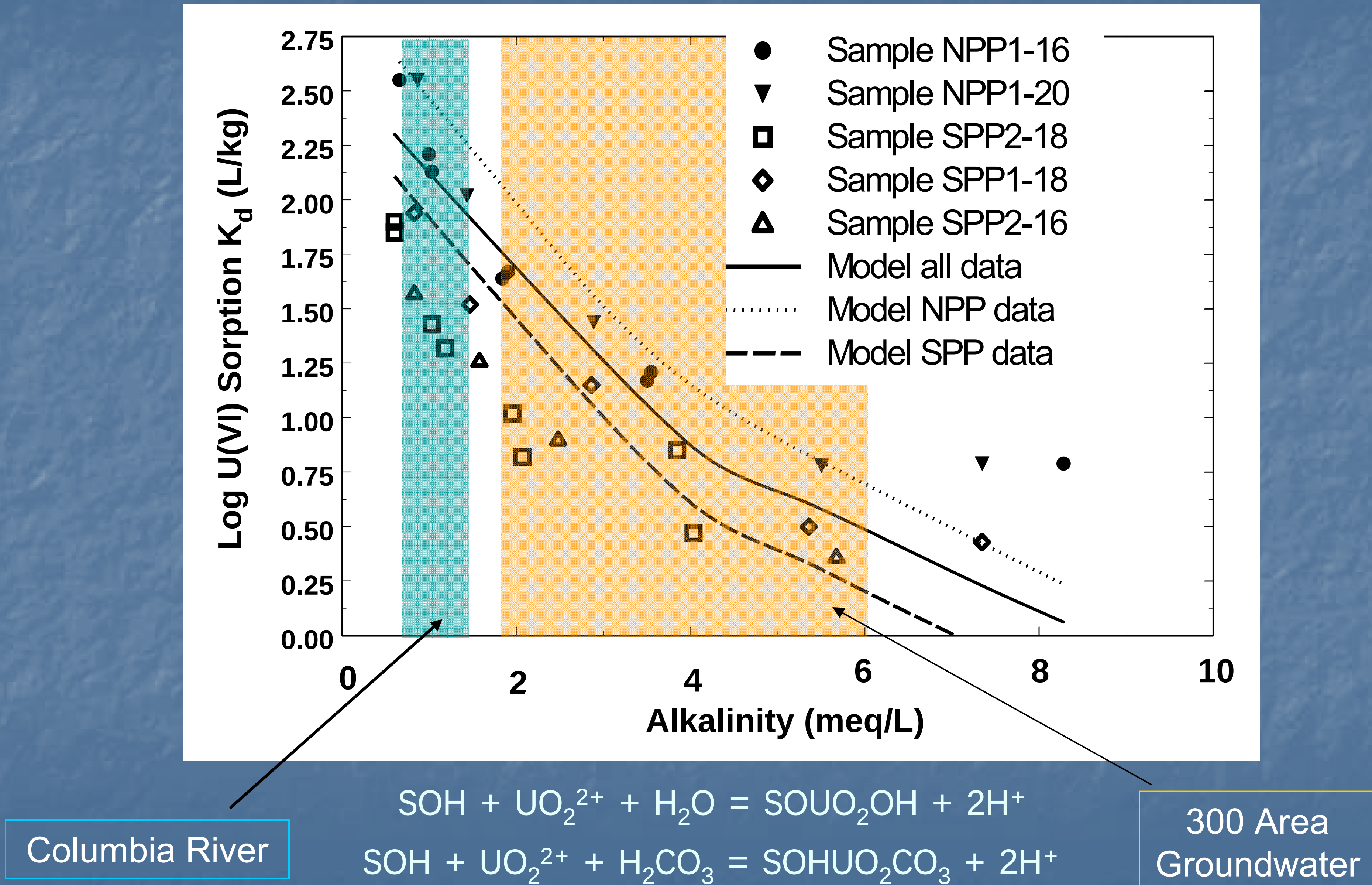
Dissolved U(VI) Complexation



Columbia River

300 Area Groundwater

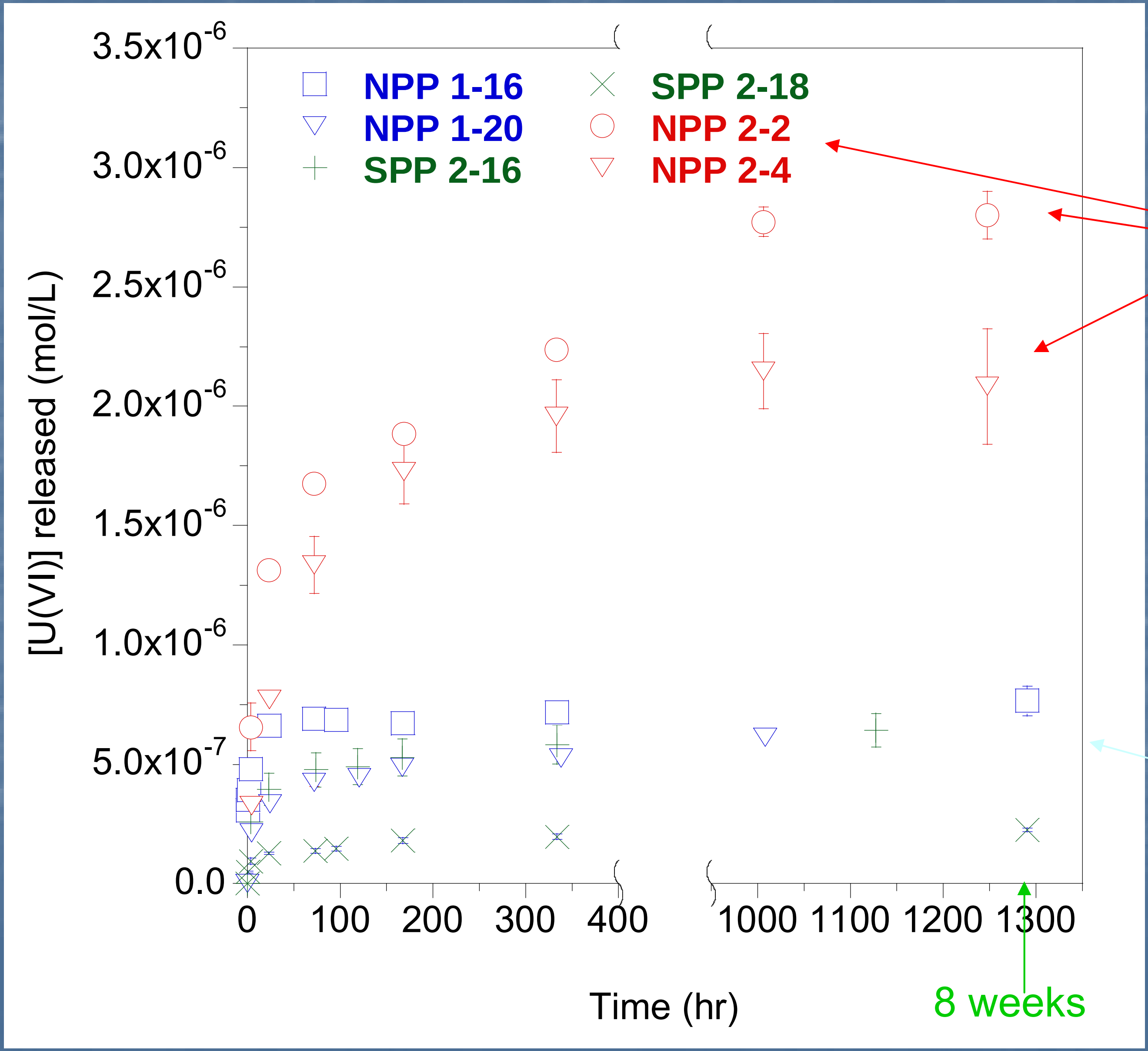
Surface Complexation Model



$$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$$

$$SOH + UO_2^{2+} + H_2CO_3 = SOHUO_2CO_3 + 2H^+$$

U(VI) Release from Hanford Solids



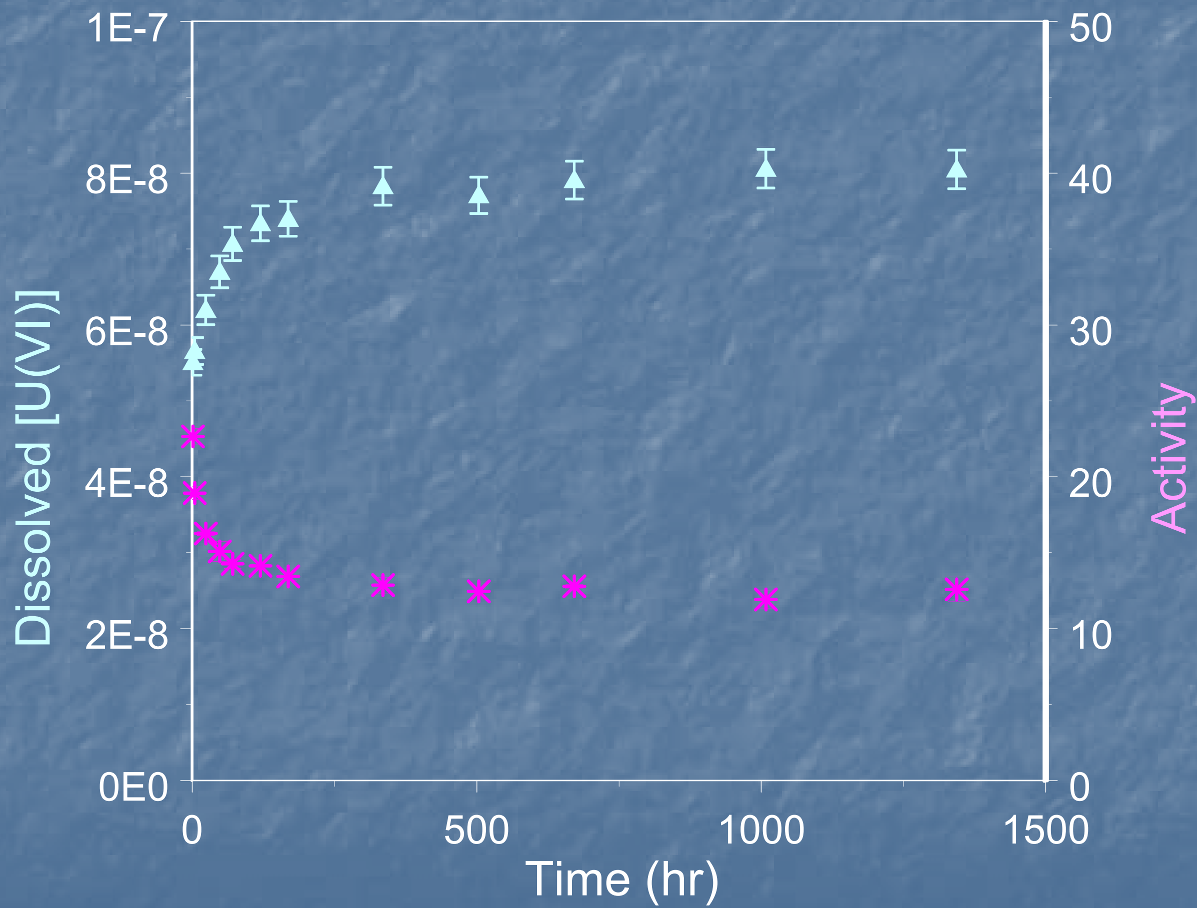
High U samples, (25 g/L)

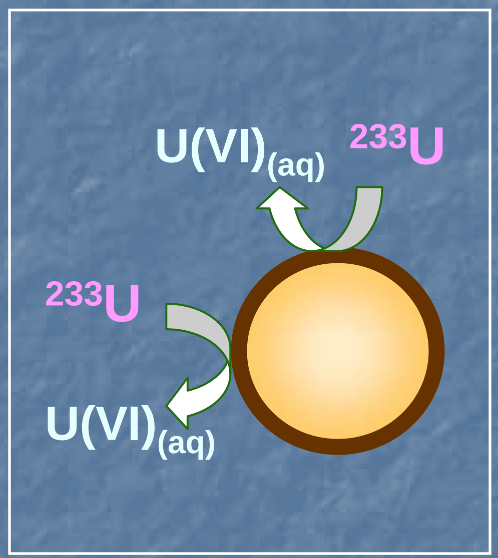
What controls U(VI) release?

Fast and slow desorption? dissolution?

Low U samples, (100 g/L)

Isotopic Exchange
a measurement of available U

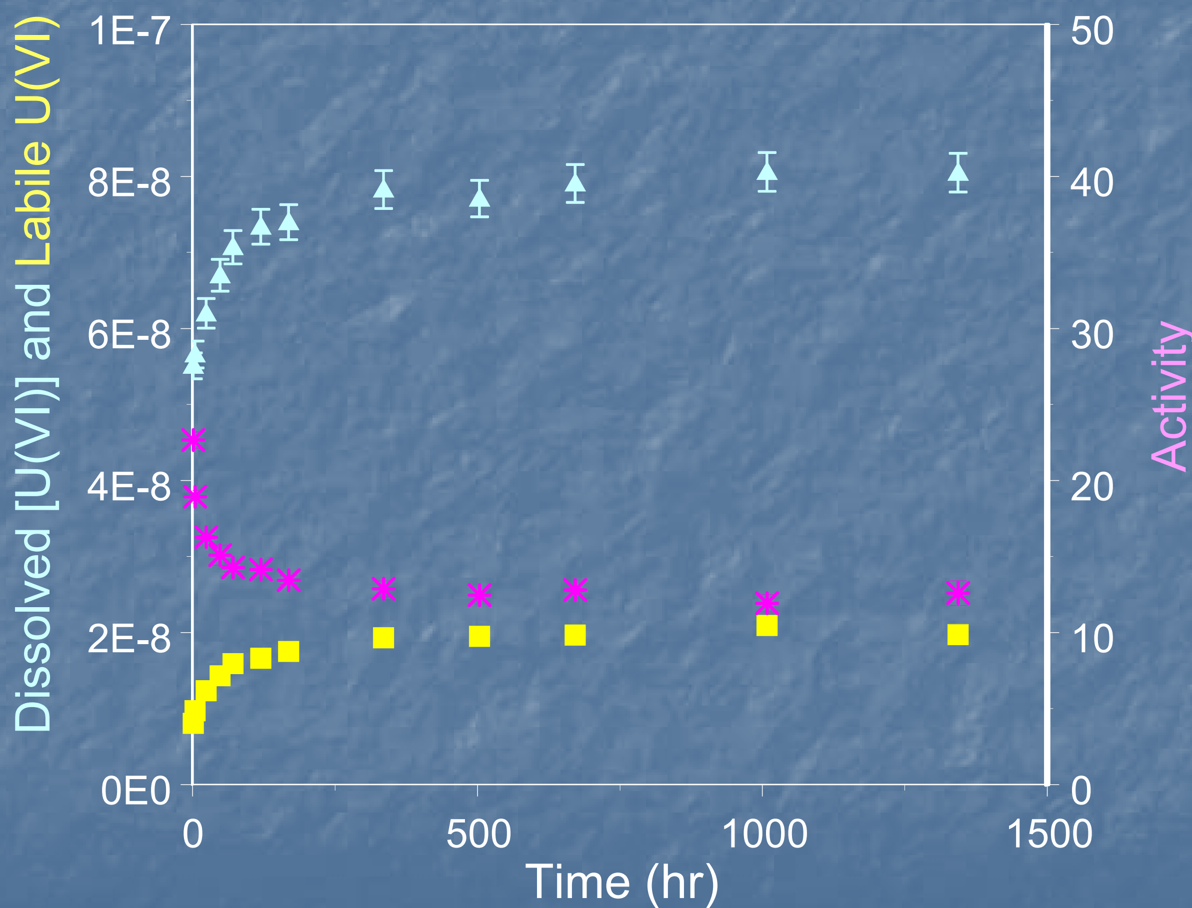


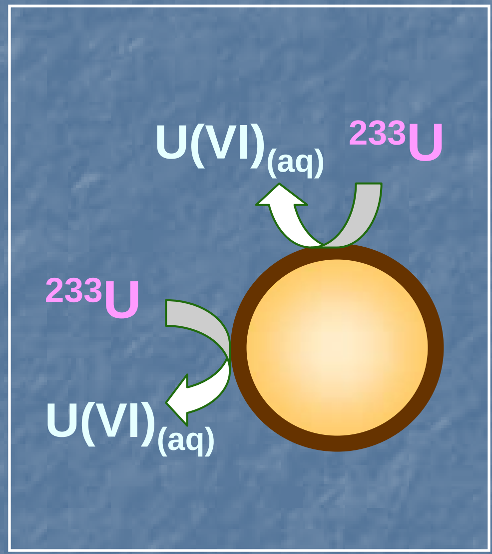


Isotopic Exchange and “Labile U”

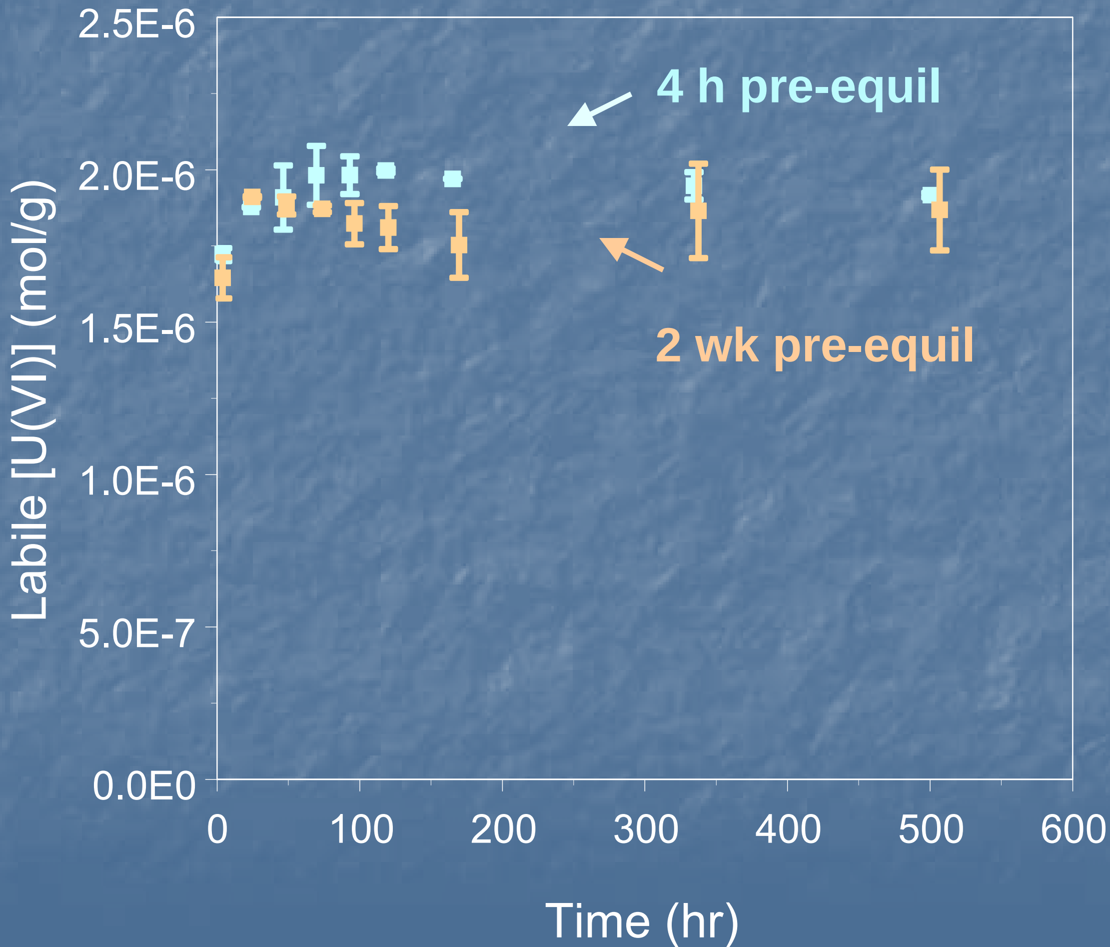
$[U(VI)]_{Labile} = (A_{System}/A) \times [U(VI)]_{diss}$

Operationally defined





^{233}U Exchange in Model Systems
Fast Desorption



U(VI) Desorption from Hematite

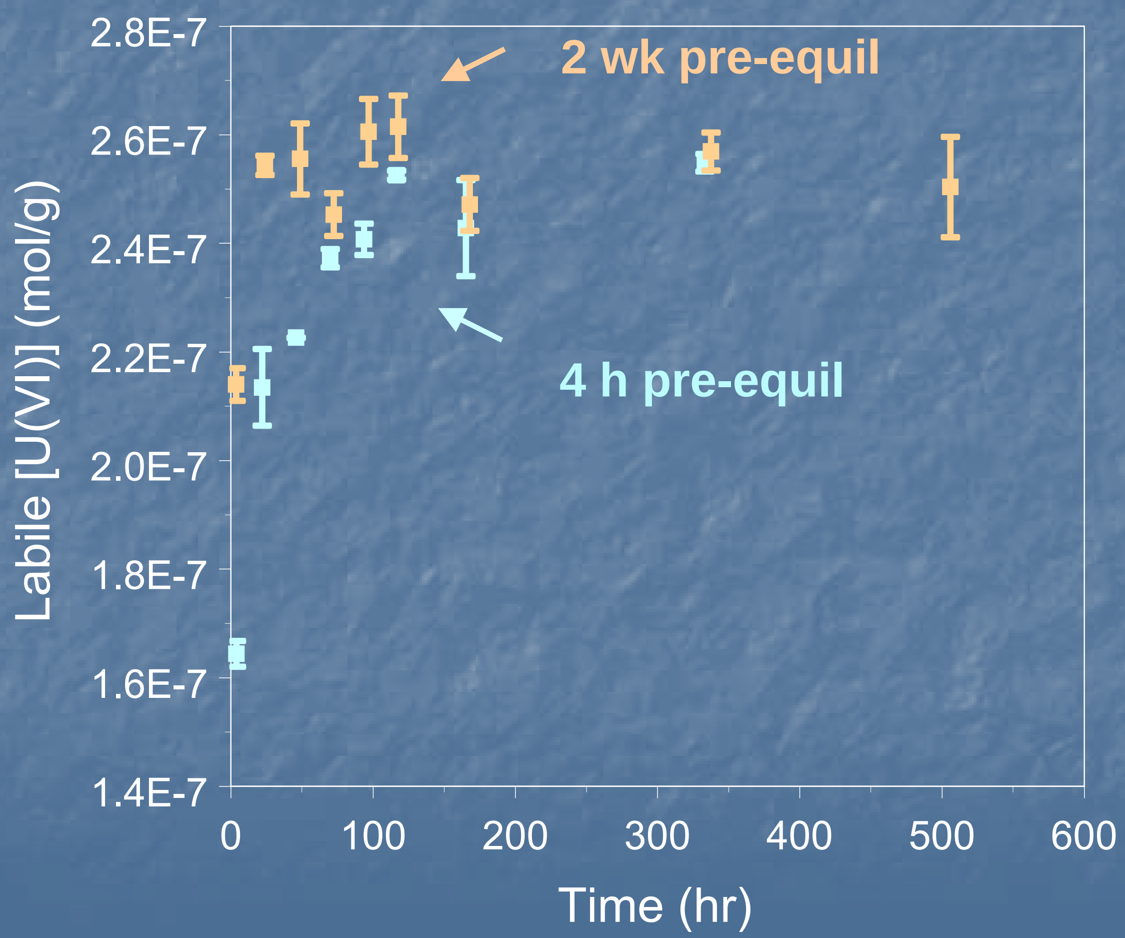
Coupled with ^{233}U Exchange

~1 uM U(VI), 48 h sorption, 4 h or 336 h desorption

pH=8, alk=4 meq/L

Rapid Progression to Equality

^{233}U Exchange in Model Systems Fast/Slow Desorption



U(VI) Desorption from Ferrihydrite

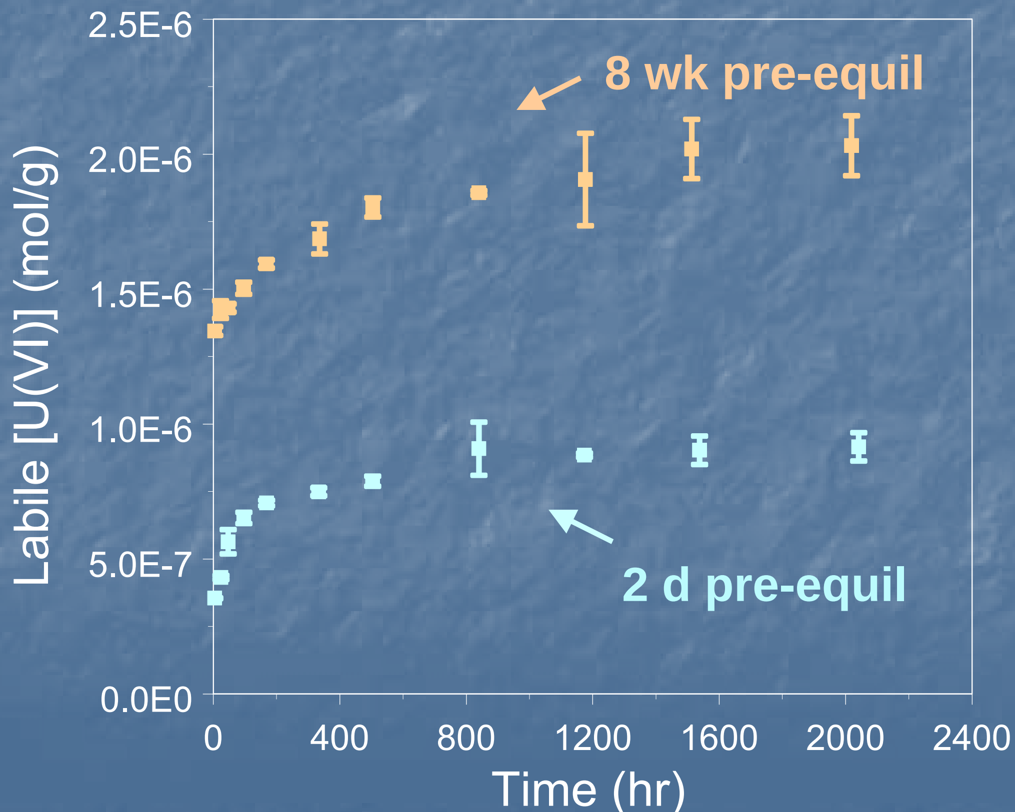
Coupled with ^{233}U Exchange

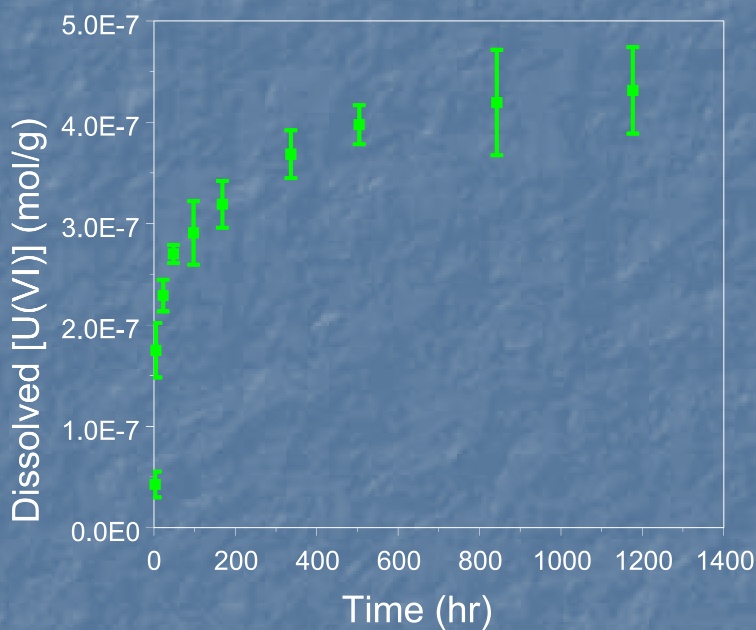
Slower Progression to Equality as U(VI) slowly desorbs from the amorphous oxide

^{233}U Exchange in Model Systems
Slow Dissolution

U(VI) Dissolution from Metatorbernite

$[Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O]$

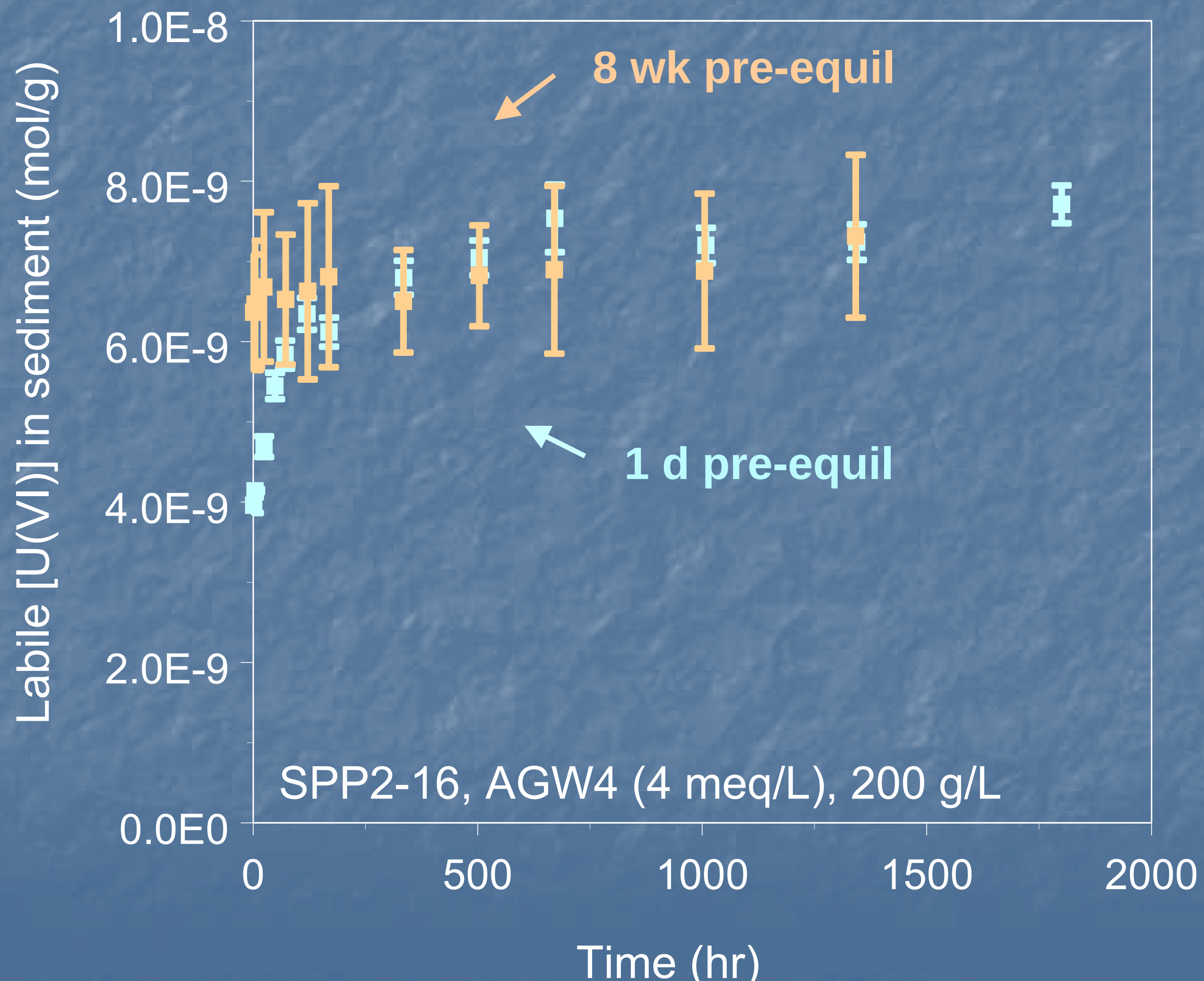




Admixed with Quartz (100 g/L)
Coupled with ^{233}U Exchange

System never reaches equality due to continual addition of U(VI)

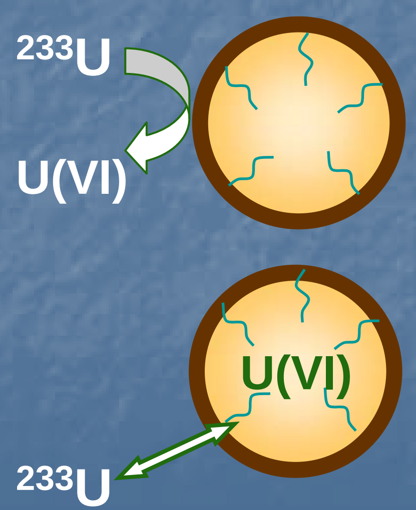
^{233}U Exchange with 300-A Sediments



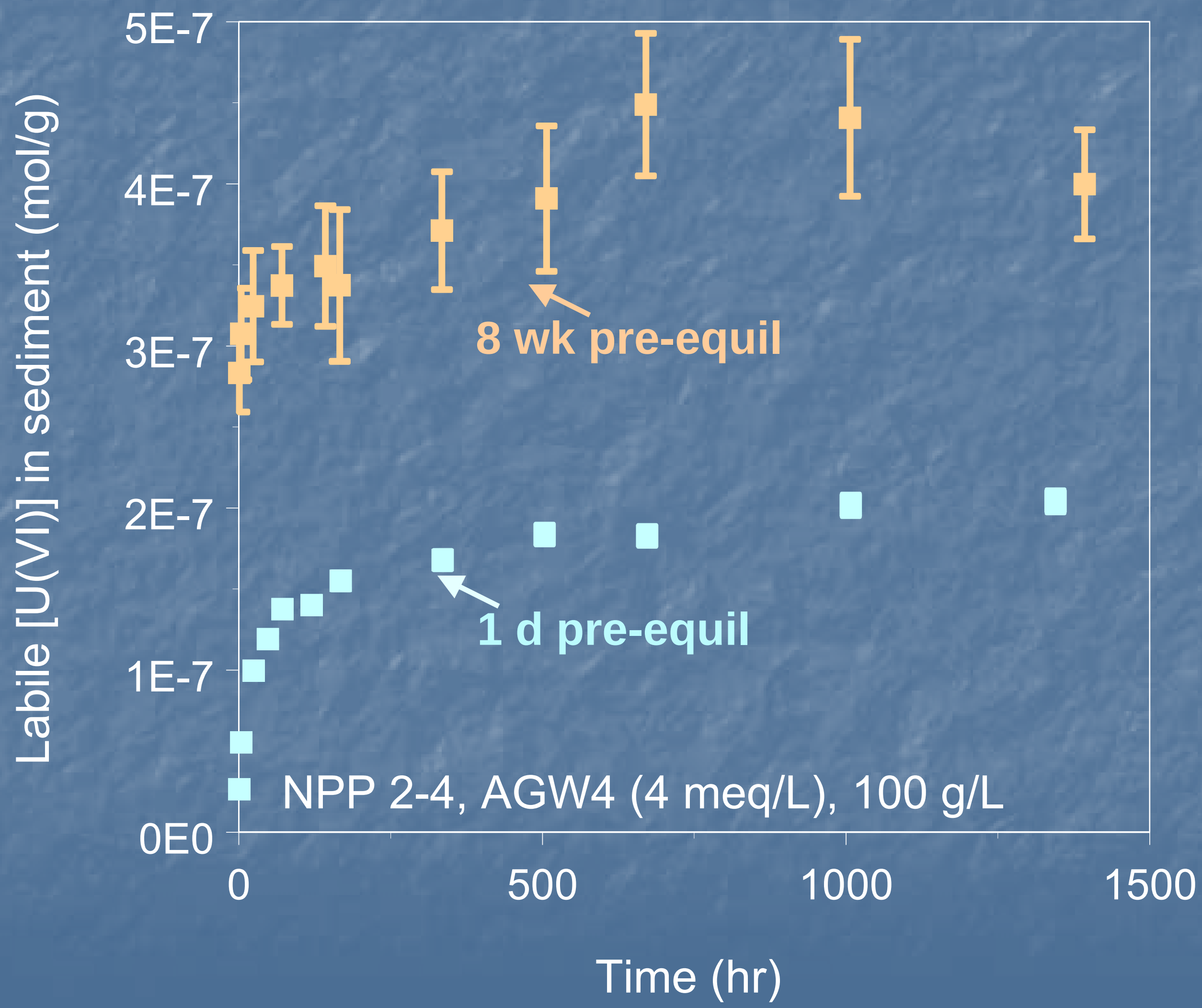
Labile U(VI) is independent of pre-equilibration time

→ indicative of desorption process

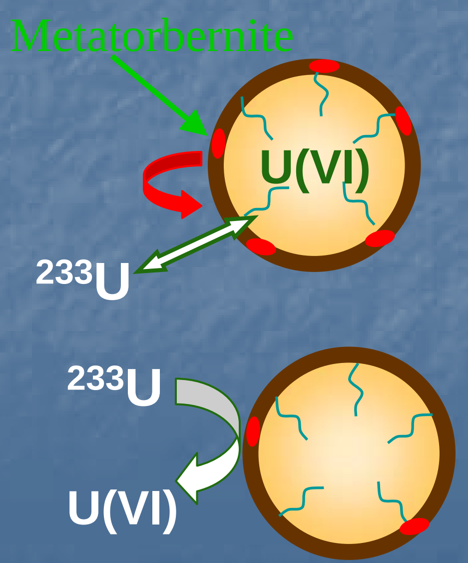
Fast and slow kinetics



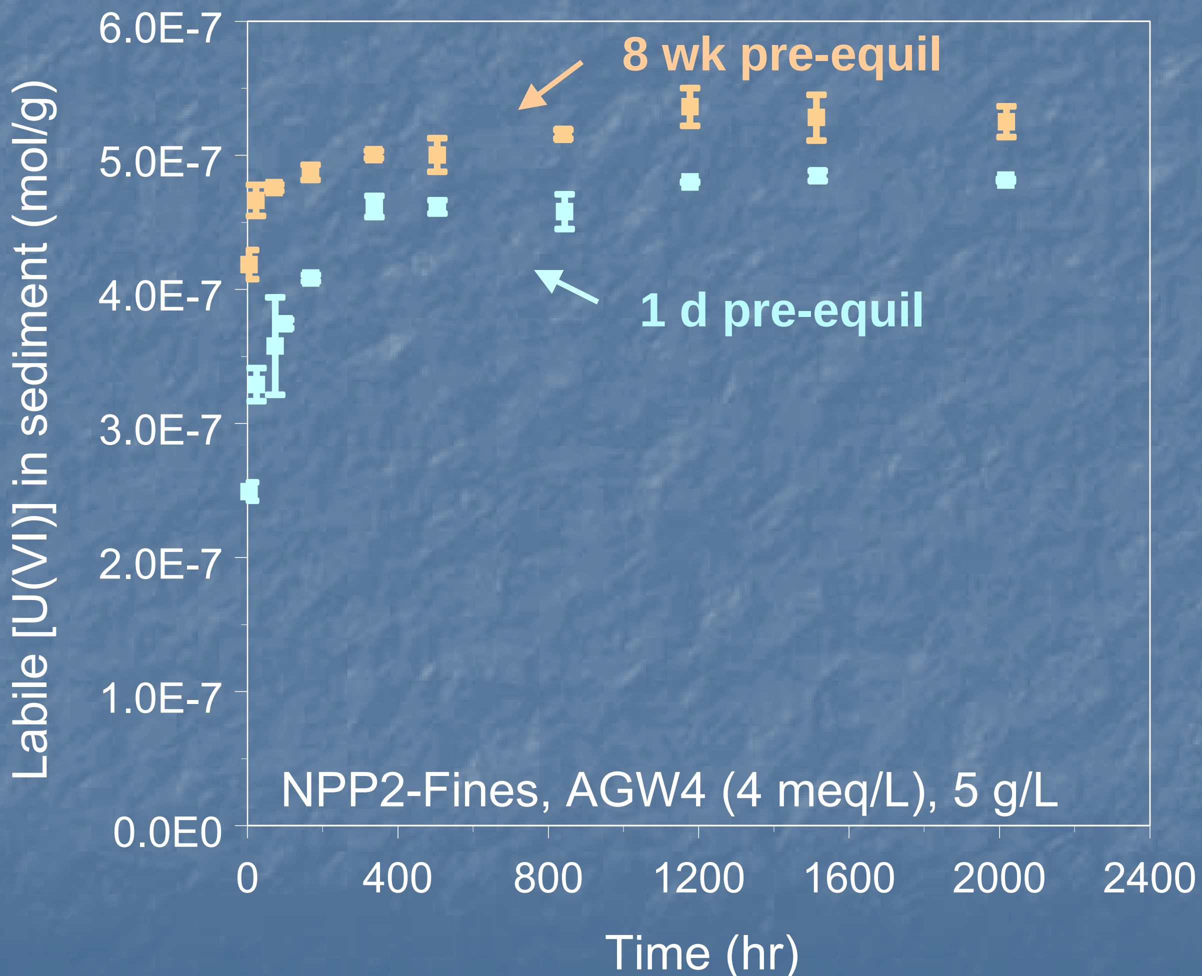
^{233}U Exchange with 300-A Sediments



U(VI) concentration increases slowly
→ labile U(VI) calculation depends on pre-equilibration time
→ indicative of dissolution process



^{233}U Exchange with 300-A Sediments



Groundwater Fines also contain a possible precipitated form of U(VI) in addition to sorbed phase

Consistent with spectroscopic studies suggesting metatorbernite and cuprosklodowskite $Cu[(UO_2)(SiO_2OH)]_2 \cdot 6(H_2O)$ in GW Fines (Singer, 2007)

Chemical Extraction of Sediment Samples

Desorb U(VI) due to higher pH and carbonate complexation

Determine labile fraction of total sediment U(VI); adsorption-desorption; dissolution-reprecipitation

Desorb and dissolve U(VI) due to buffered, lower pH

Sample	(Bi)carbonate Extraction % of U_{tot} [a]	Isotopic Exchange % of U_{tot} [b]	Formate Extraction % of U_{tot} [c]	Formate Extraction % of Cu_{tot} [c]
SPP 1-18	36 ± 1	36 ± 1	79 ± 3 *	4 ± 0.1
SPP 2-16	42 ± 4	41 ± 2	93 ± 3 *	3 ± 0.1
NPP 1-20	30 ± 0.5	36 ± 1	78 ± 3 *	14 ± 1
NPP 2-4	29 ± 1	88 ± 9	**80 ± 2**	**91 ± 5**

Labile fraction = desorbed fraction for deep vadose zone samples

Labile fraction ≠ desorbed fraction for samples with metatorbernite

a. pH = 9.45, alk = 20 meq/L, 72 h; b. pH = 7.9 – 8.3, alk = 4 meq/L, 336h (1260h pre-equil in AGW); c. pH 3.5, 72 h, 0.5 M

Chemical Extraction of Sediment Samples

Desorb U(VI) due to higher pH and carbonate complexation

Determine labile fraction of total sediment U(VI); adsorption-desorption; dissolution-reprecipitation

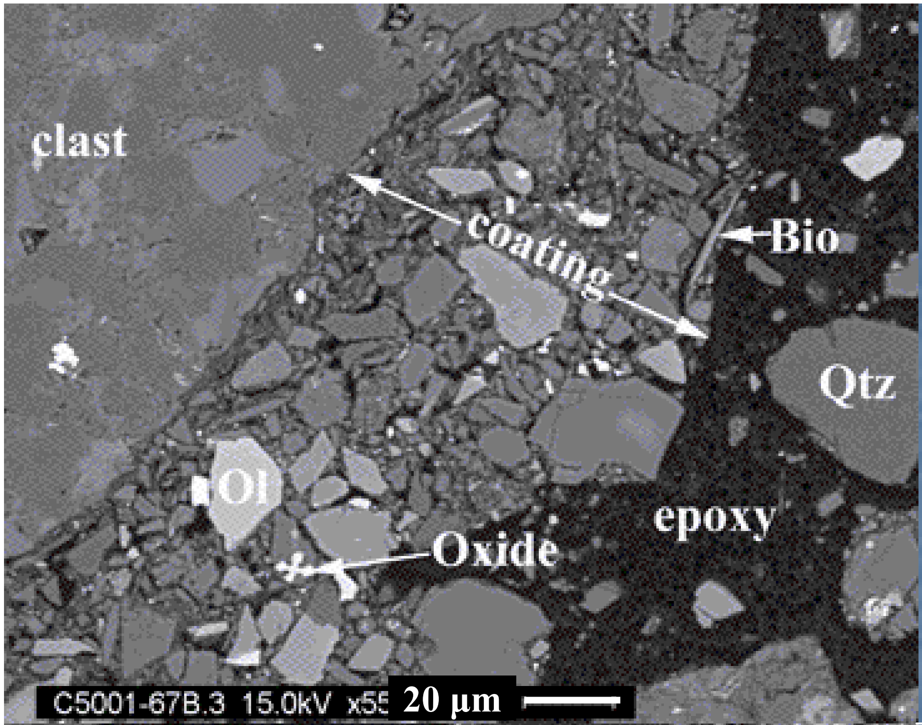
Desorb and dissolve U(VI) due to buffered, lower pH

Sample	Bicarbonate Extraction % of U_{tot}	Isotopic Exchange % of U_{tot}	Formate Extraction % of U_{tot}	Formate Extraction % of Cu_{tot}
SPP 1-18	36 ± 1	36 ± 1	79 ± 3 *	4 ± 0.1
SPP 2-16	42 ± 4	41 ± 2	93 ± 3 *	3 ± 0.1
NPP 1-20	30 ± 0.5	36 ± 1	**78 ± 3** *	**14 ± 1**
NPP 2-4	29 ± 1	88 ± 9	**80 ± 2**	**91 ± 5**

Low pH dissolves most of Cu_{tot}; likely dissolves most of metatorbernite; deep samples don't have metatorbernite

Low pH releases large fraction of U_{tot}; dissolution of grain coatings releases co-precipitated U(VI) that is not "labile"?

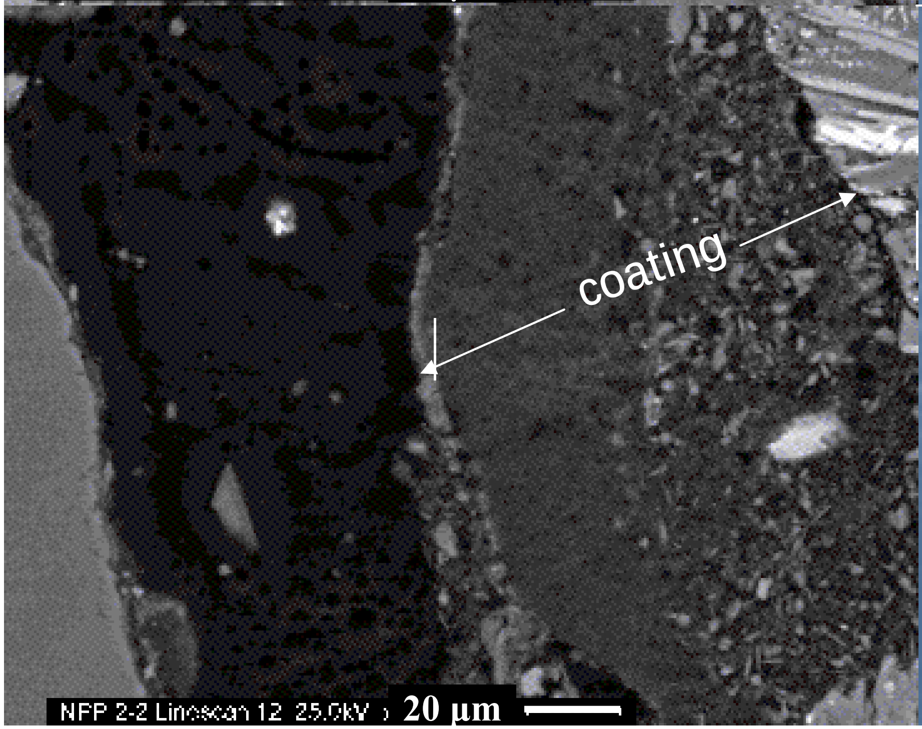
* remaining U is < 1.5 ppm, ~ equivalent to bkg



Hanford <u>uncontaminated</u> vadose zone sample: C5001-67B

Coating consists of micron-sized mineral fragments.

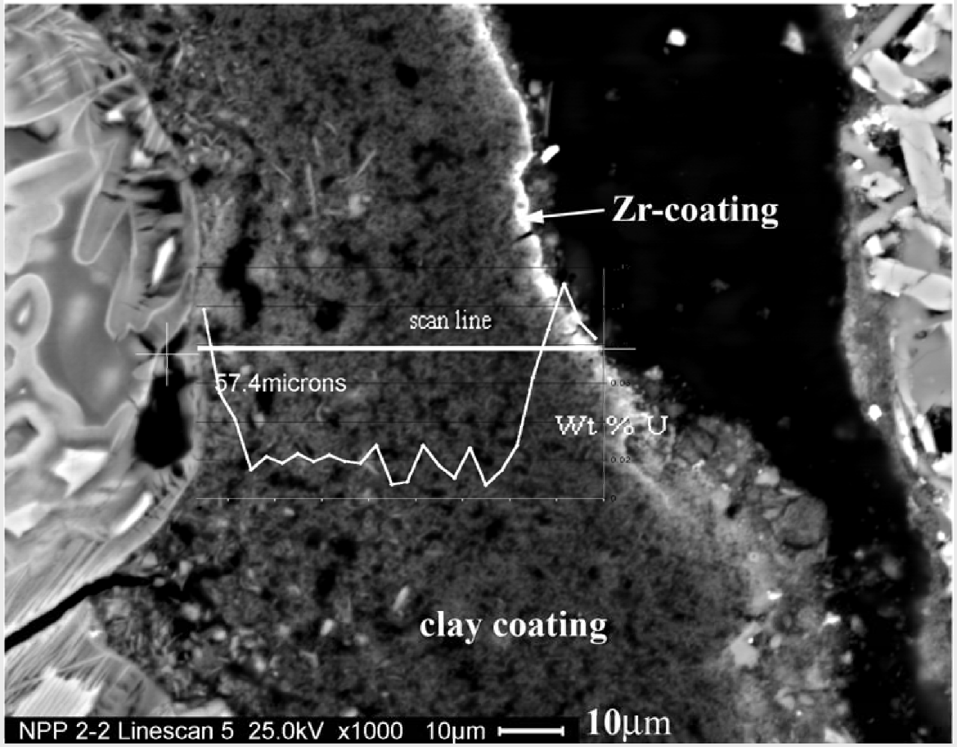
Stubbs et al., 2008

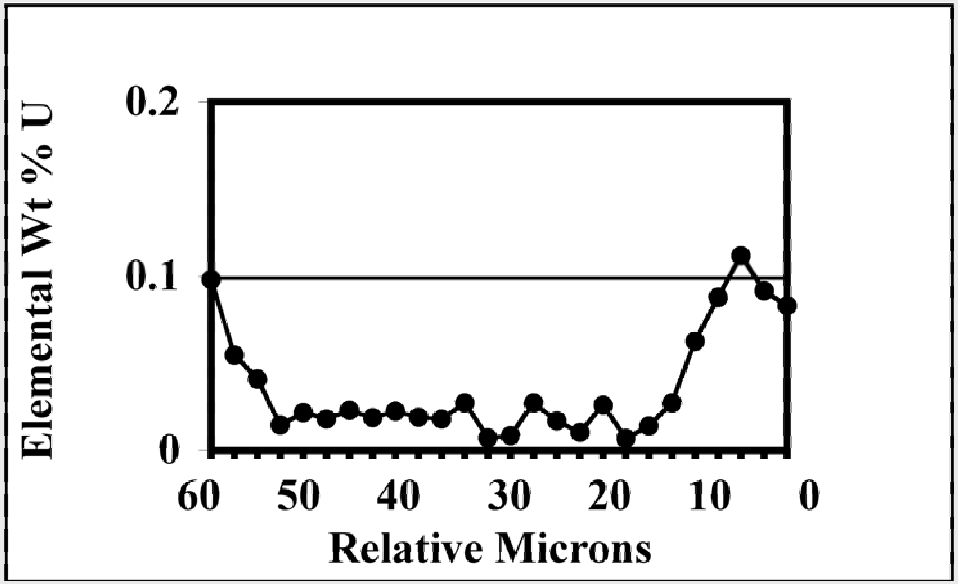


Hanford <u>contaminated</u> vadose zone sample: NPP2-2

Coatings have finer texture, with fine-grained clay rind several microns thick.

May be influenced by infiltration of variable pH water with high concentrations of Al and Si.





Hanford contaminated vadose zone sample: NPP2-2

Backscattering image of a 60 µm wide, fine-grained clay coating.

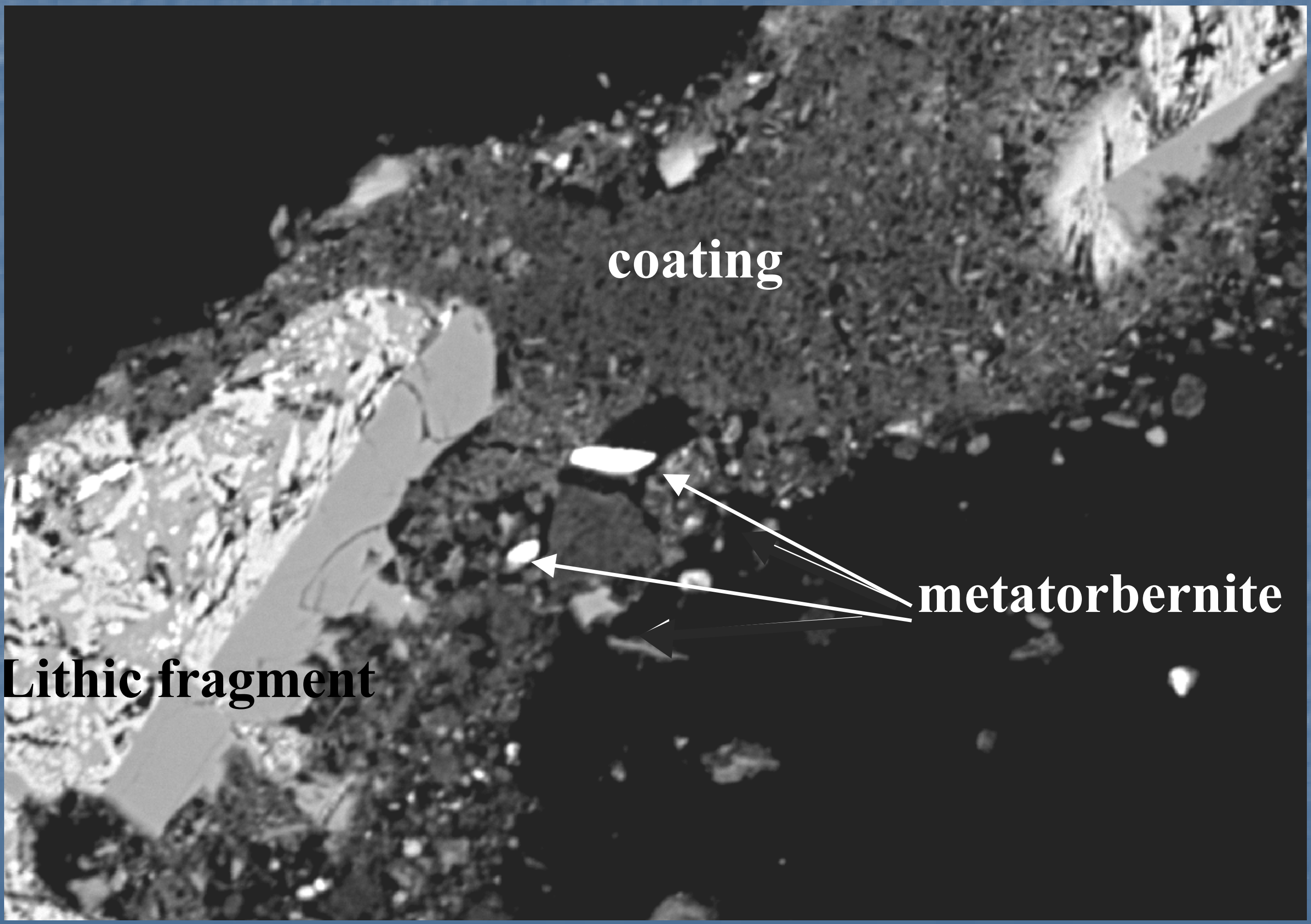
Outer edge of coating: very high concentrations of Zr and U, presumably from cladding waste.

Electron microprobe WDS linescans show gradients in U concentration across the coating.

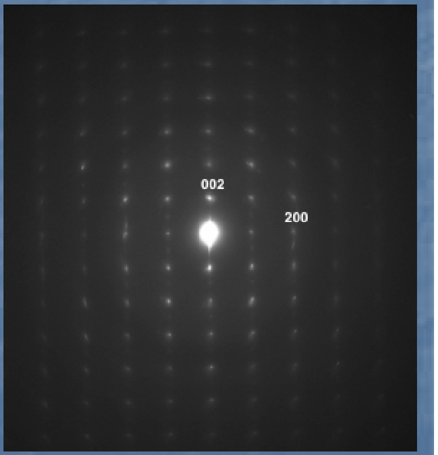
Stubbs et al., 2008

Hanford contaminated vadose zone sample

Metatorbernite precipitate [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$]
encapsulated within coatings on contaminated grains



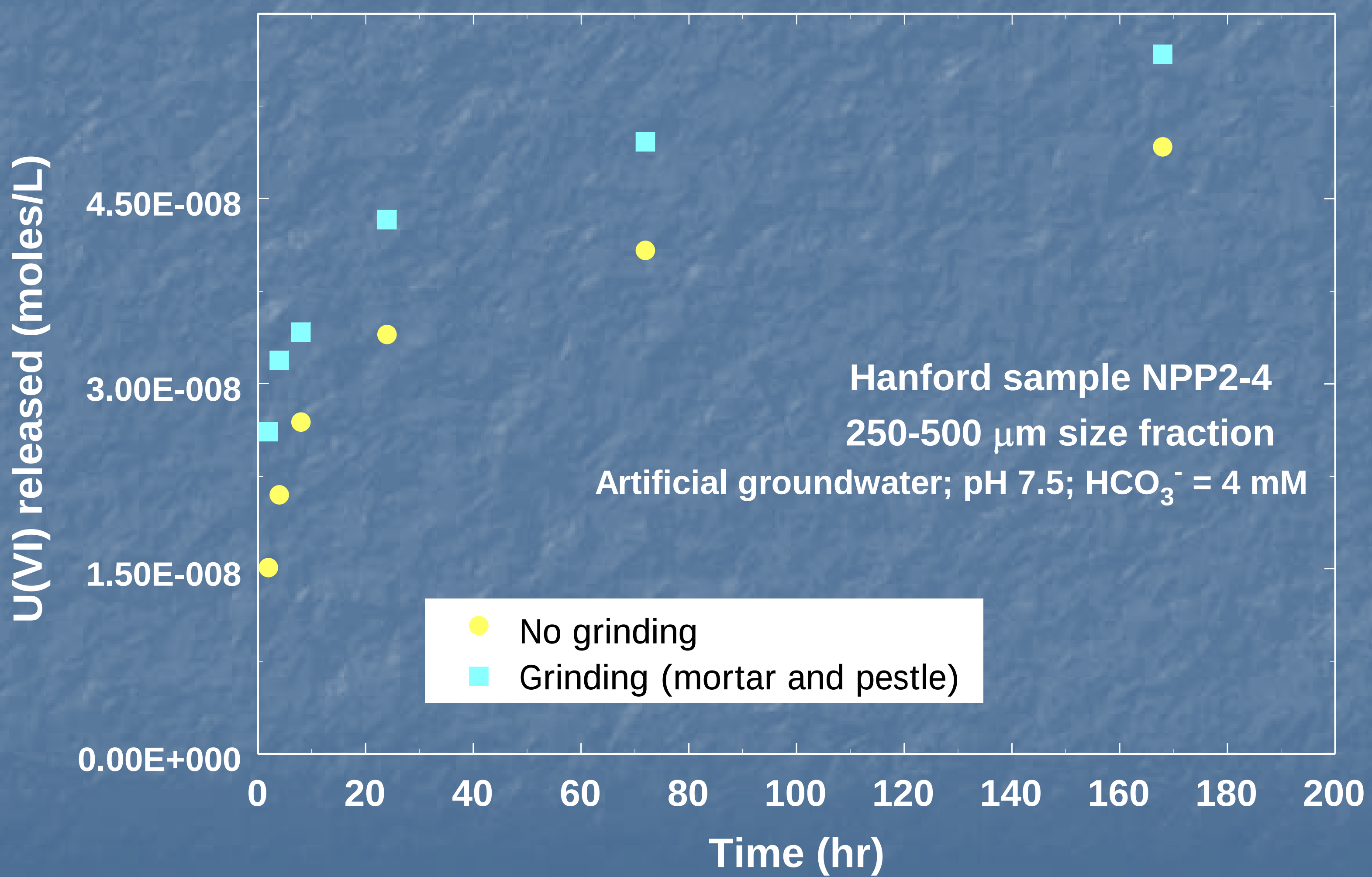
NPP 2-2



(Bi)carbonate extraction does not appear to remove U in metatorbernite, Zr-rinds, clay coating, void linings

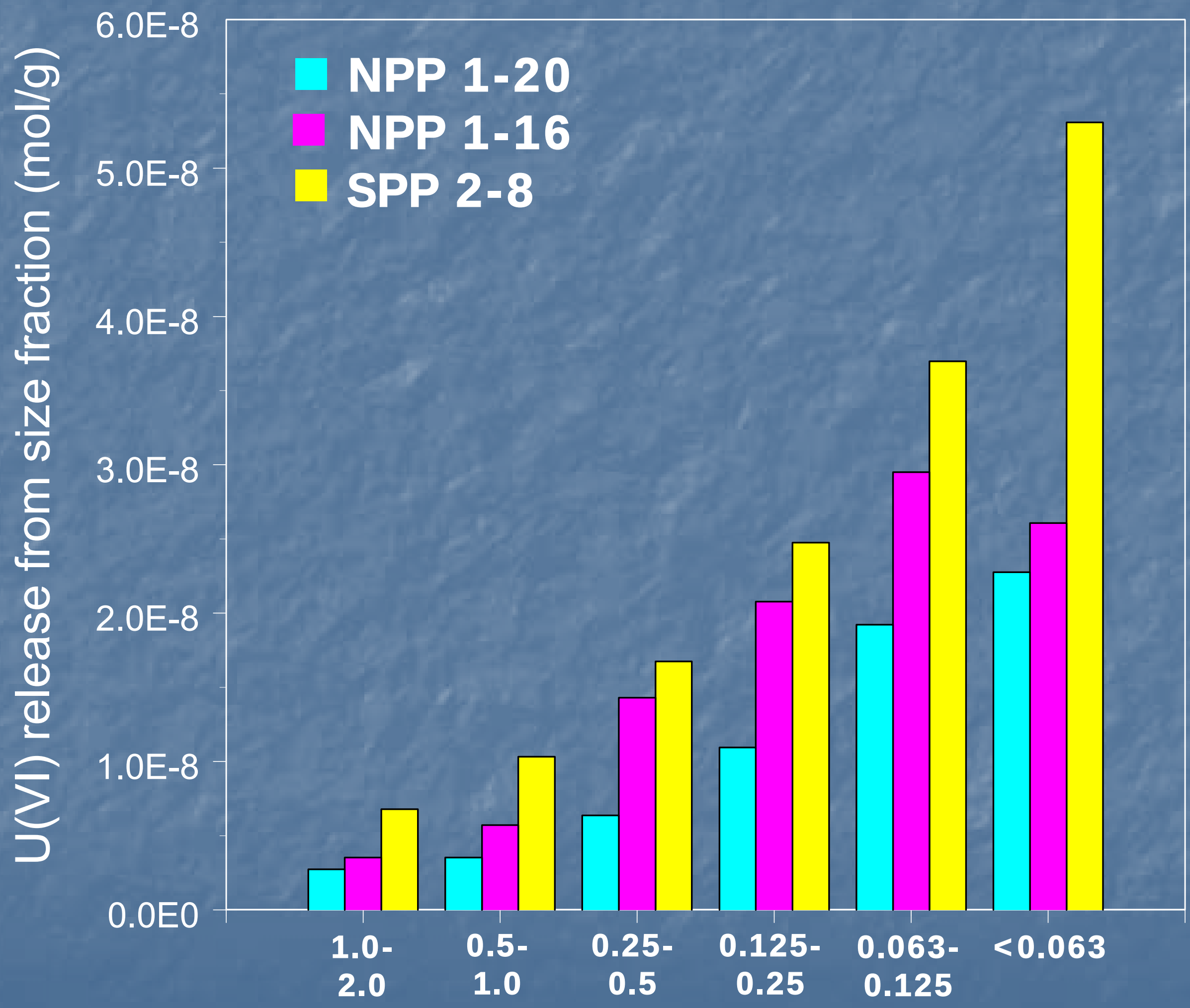
Stubbs et al., 2008

Hanford contaminated vadose zone sample: NPP2-4



Arai et al., 2008

U(VI) Release from Size-Fractions of 300-Area Sediments (<2 mm)

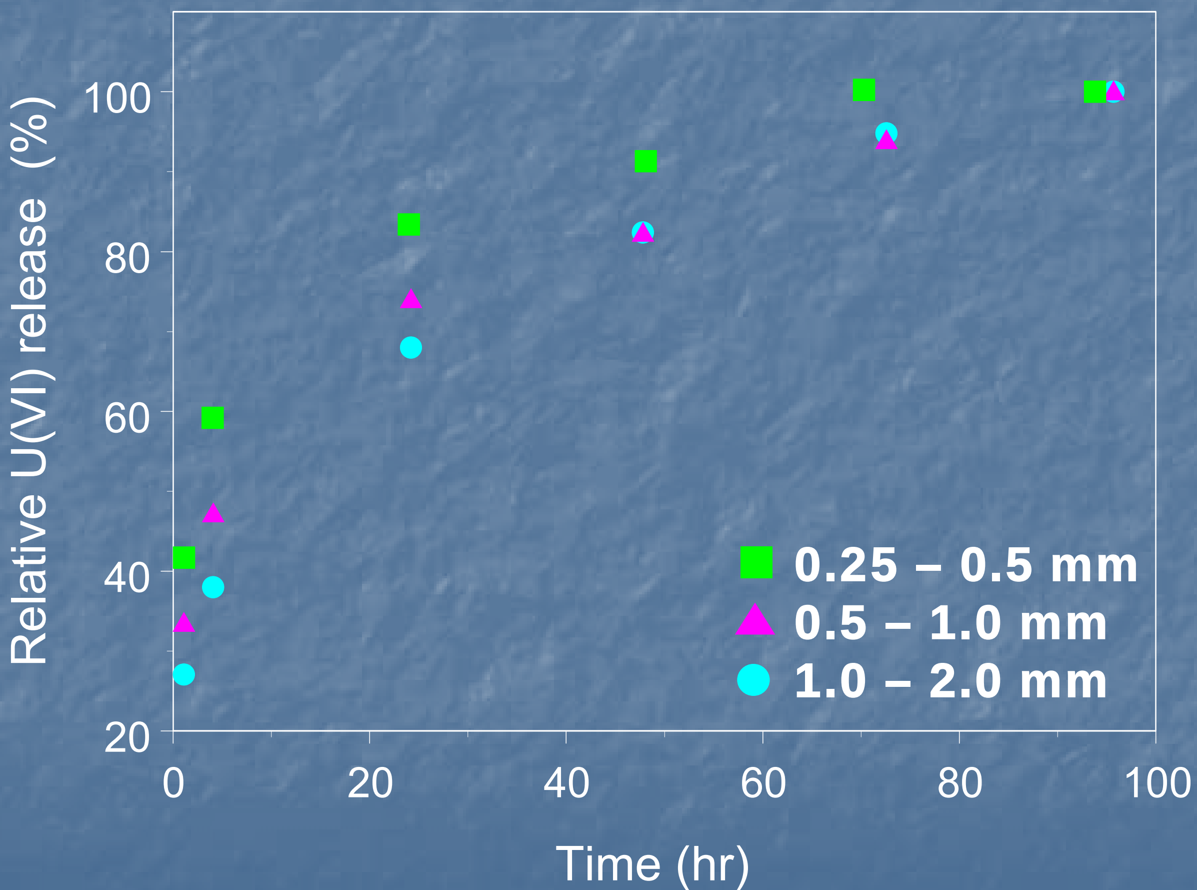


After 24 hr reaction with AGW 4 (4 meq/L)

Smaller grains release U(VI) rapidly to solution

>0.5 – 1 mm: 100 g/L, 0.25 – 0.5 mm: 25 g/L, 0.125 – 0.25 mm: 10 g/L, <0.125: 2 g/L

U(VI) Release from Size-Fractions of 300-Area Sediments (<2 mm)



Three largest size fractions account for nearly 100% of U(VI) release

Smaller size fractions have rapid kinetics and reach steady state on short time scale

Larger size fractions have slow release over time suggesting mass transfer limitations

SPP 2-8

Part II:

Grain-scale porosity and diffusion in Hanford 300 Area sediments

Experiments and Modeling

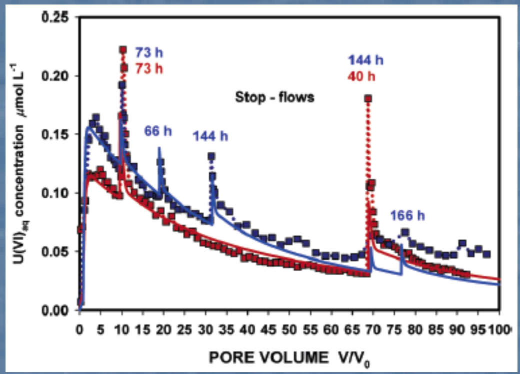
Uranium interaction with Hanford sediments exhibits <u>kinetic</u> (<u>*diffusion*</u>) <u>limitation</u>

- Chemical extractions are rate limited
  - Deeper sediments (desorption): Diffusion kinetics
  - Upper sediments (dissolution): Chemical <u>and</u> diffusion kinetics

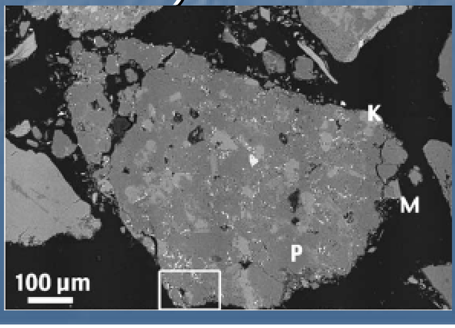
- ^{233}U isotope exchange experiments

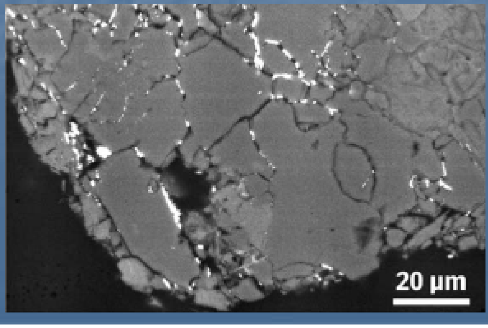
- Release rate is dependent on size fraction
  - Faster release with smaller size fraction
  - Function of diffusion path length?

- "U(VI) release and transport... are kinetically controlled."
  - SPP2-18 sediments; Qafoku et al., ES&T, 2005)

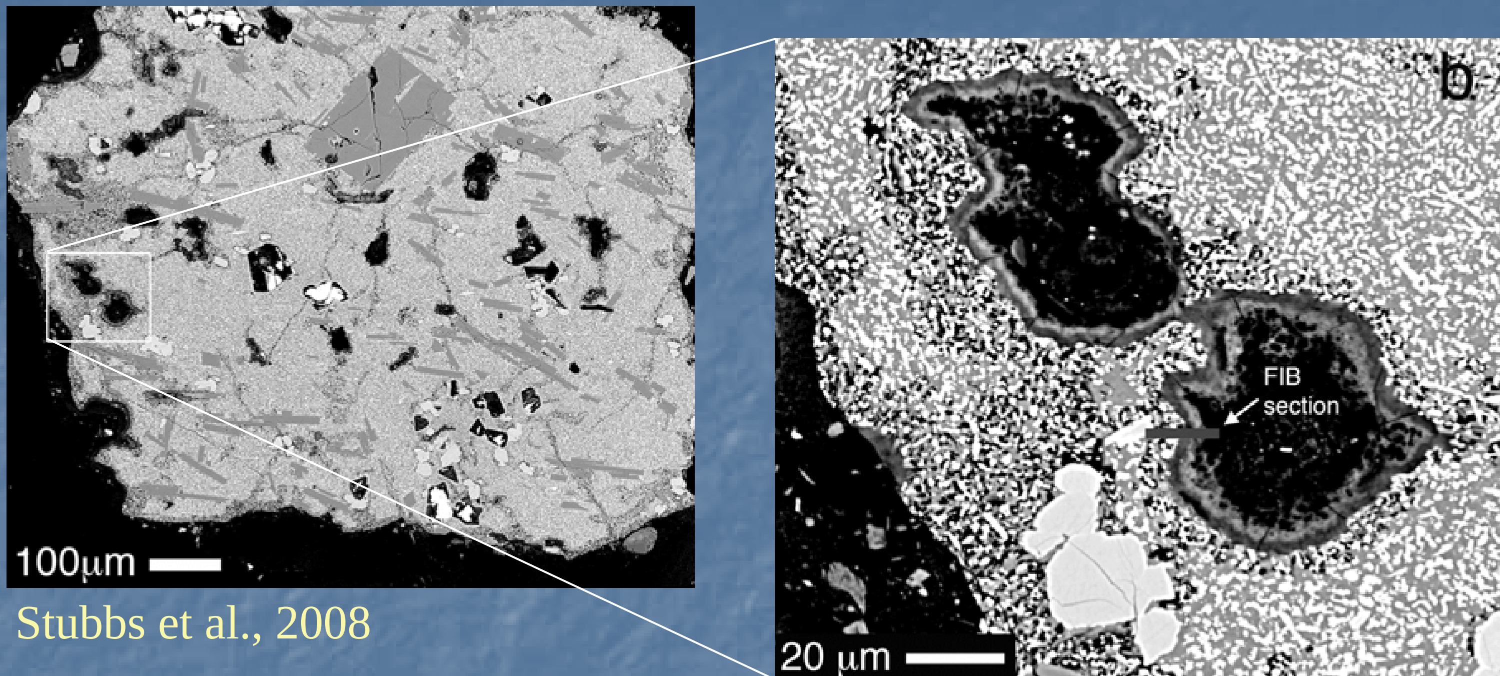


- Diffusion limitation observed (and modeled) in other Hanford sediments
  - BX-102 sediments:
    Liu et al., 2004, 2006
    McKinley et al., 2006
    Ilton et al., 2008





Microscale Diffusion



Stubbs et al., 2008

Goals: Determine properties of microscale diffusion domain

Grain aggregates, clay coatings, grain fractures
("Intragranular" pore space)

- Intragranular pore volume
- Exchange rates and behavior

Method: <u>High</u> <u>resolution</u> non-reactive flow-interruption tracer studies

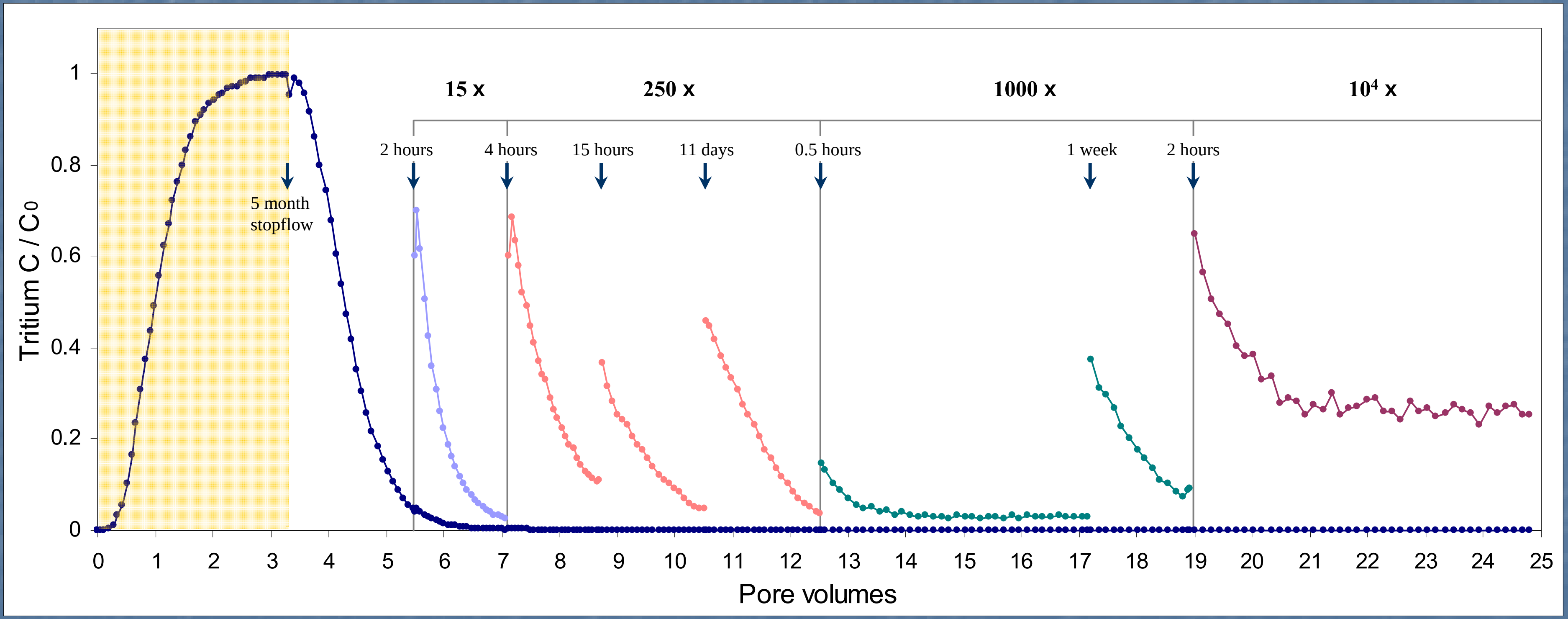
300-A Column Tracer Studies: Experiment

- Methodology (Deb Stoliker)
  - r = 1.1 cm, h = 5-15 cm, n = 50%
  - Loaded with ^3H in AGW
    - 1.7×10^6 dpm/mL (750 nCi/mL)
    - $C_0 > 10^4 \times$ detection limit
  - Sealed and stored for ~5 mo
  - Eluted with non-tracer AGW
  - ~8 stopflows: hours to days
- Various 300-A sediments:

NPP 1-8	SPP 1-18
NPP 1-16	SPP 2-16
NPP 2-4	SPP 2-18

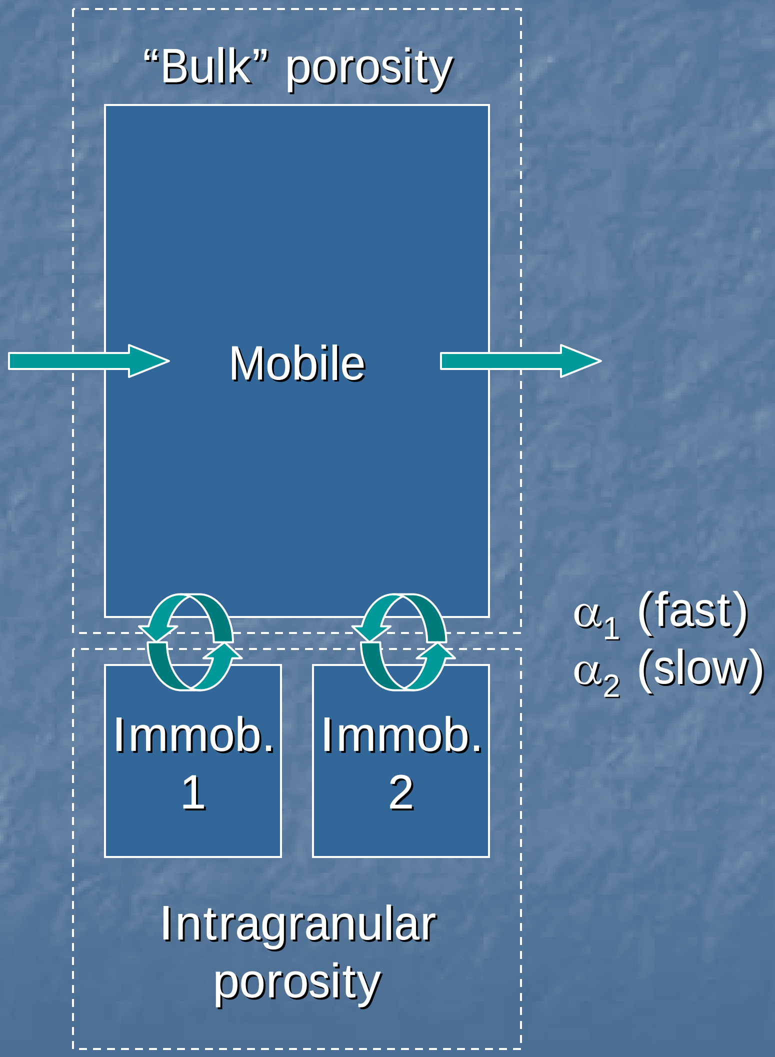
300-A Column Tracer Studies: Experiment

SPP2-16:



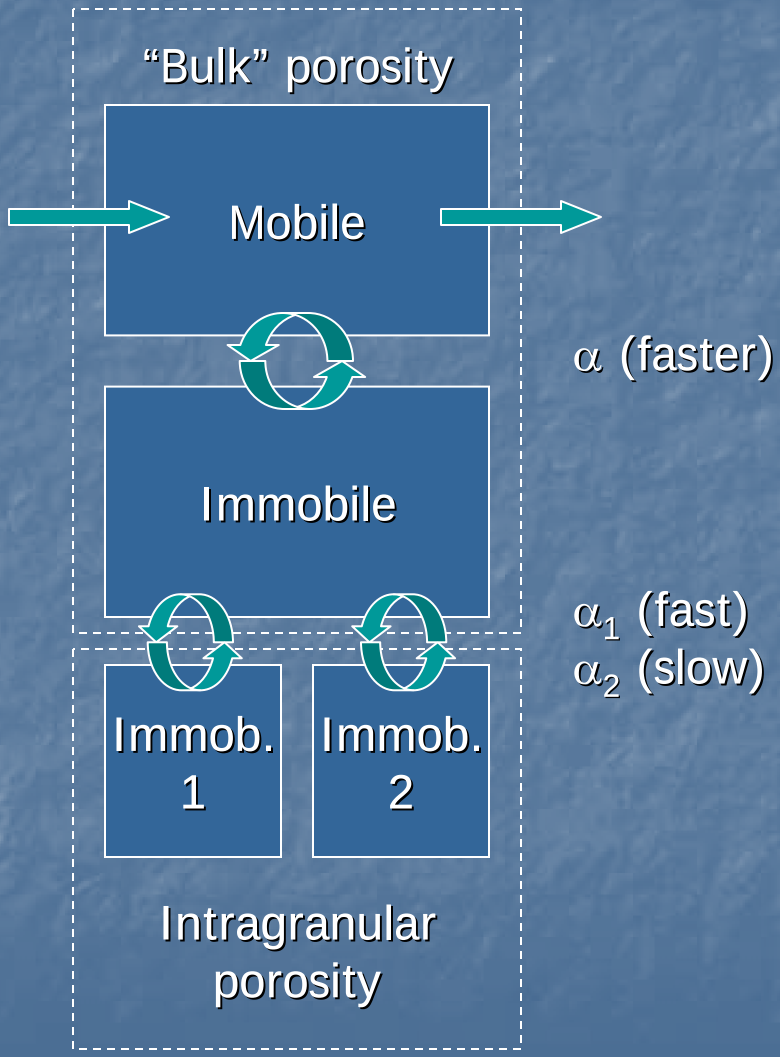
300-A Column Tracer Studies: Modeling

- Methodology
  - Multi-rate first order mass exchange
  - Dispersion coefficient fit from breakthrough and first elution (CXTFIT)
  - Rebounds modeled using PHREEQC
    - Two rates (zones) used to describe “intragranular” porosity
    - Determine pore size, exchange rates

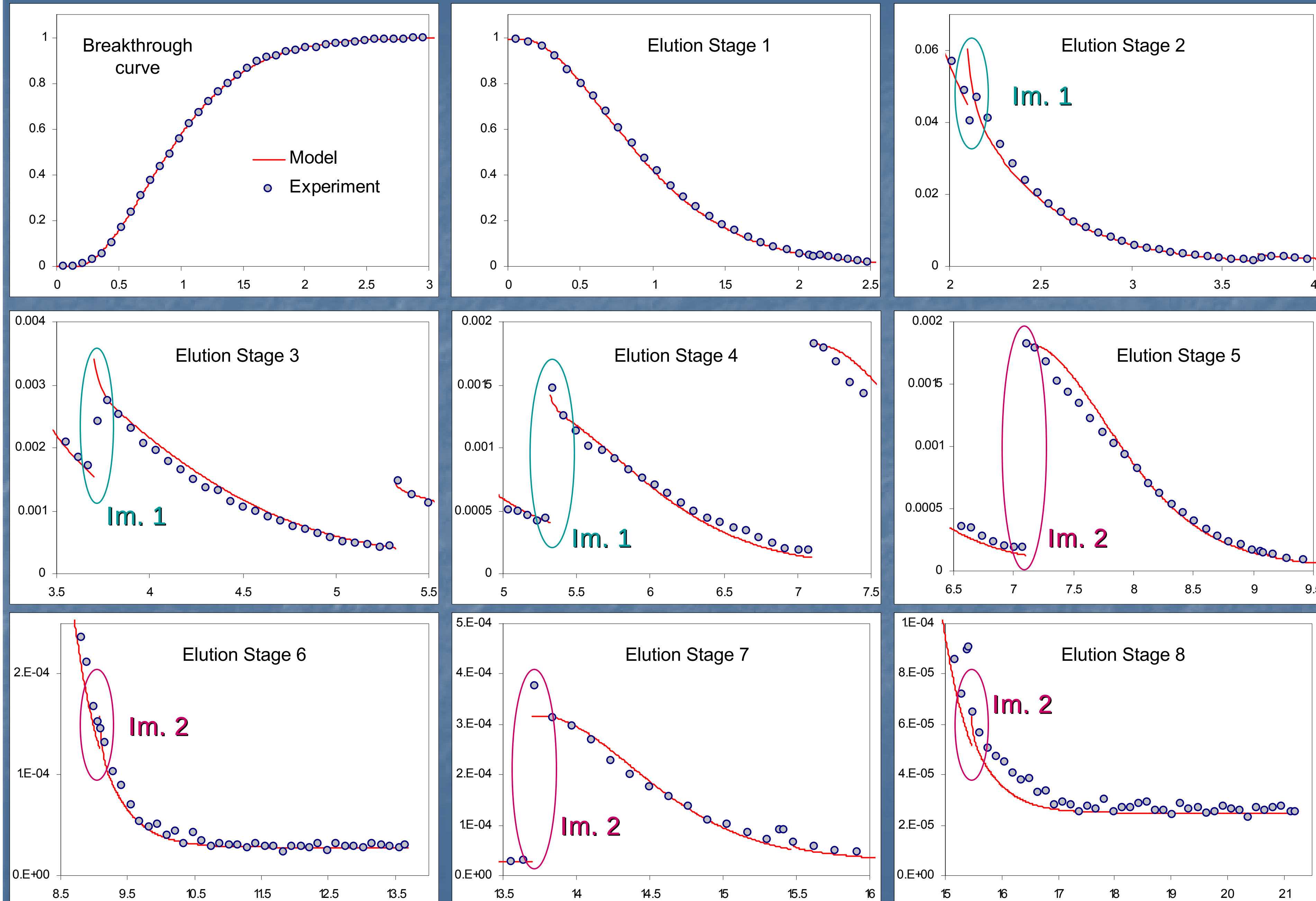


300-A Column Tracer Studies: Modeling

- Methodology
  - Multi-rate first order mass exchange
  - Dispersion coefficient fit from breakthrough and first elution (CXTFIT)
  - "Dual-porosity" model used when necessary
  - Stopflows modeled using PHREEQC
    - Two rates (zones) used to describe "intragranular" porosity
    - Determine pore size, exchange rates



Results: SPP 2-16



300-A + ^{3}H Stopflow Column Summary

	Mobile-immobile ratio (β)		Mass-exchange coefficient (α)	Intragranular porosity (θ)	% volume of sediment
NPP 2-4	1.0	region 1:	1.5×10^{-7} s^{-1}	0.003	0.60
		region 2:	3.3×10^{-9} s^{-1}	0.0022	0.45
				0.0052	1.05
SPP1-18	0.7	region 1:	1.0×10^{-6} s^{-1}	0.0091	1.67
		region 2:	3.0×10^{-9} s^{-1}	0.0016	0.29
				0.0107	1.96
SPP2-16	0.3	region 1:	1.4×10^{-7} s^{-1}	0.0025	0.40
		region 2:	1.6×10^{-9} s^{-1}	0.00096	0.16
				0.00346	0.56
SPP2-18	0.5	region 1:	1.6×10^{-6} s^{-1}	0.0200	3.18
		region 2:	2.8×10^{-9} s^{-1}	0.0020	0.32
				0.0220	3.50

- Dual porosity required, BUT stopflows insensitive to β
- Intragranular pore volume 0.5-3.5% of sediment volume
- Two rates differ by 2-3 orders of magnitude
- Slower region is relatively consistent between columns

Current and future work

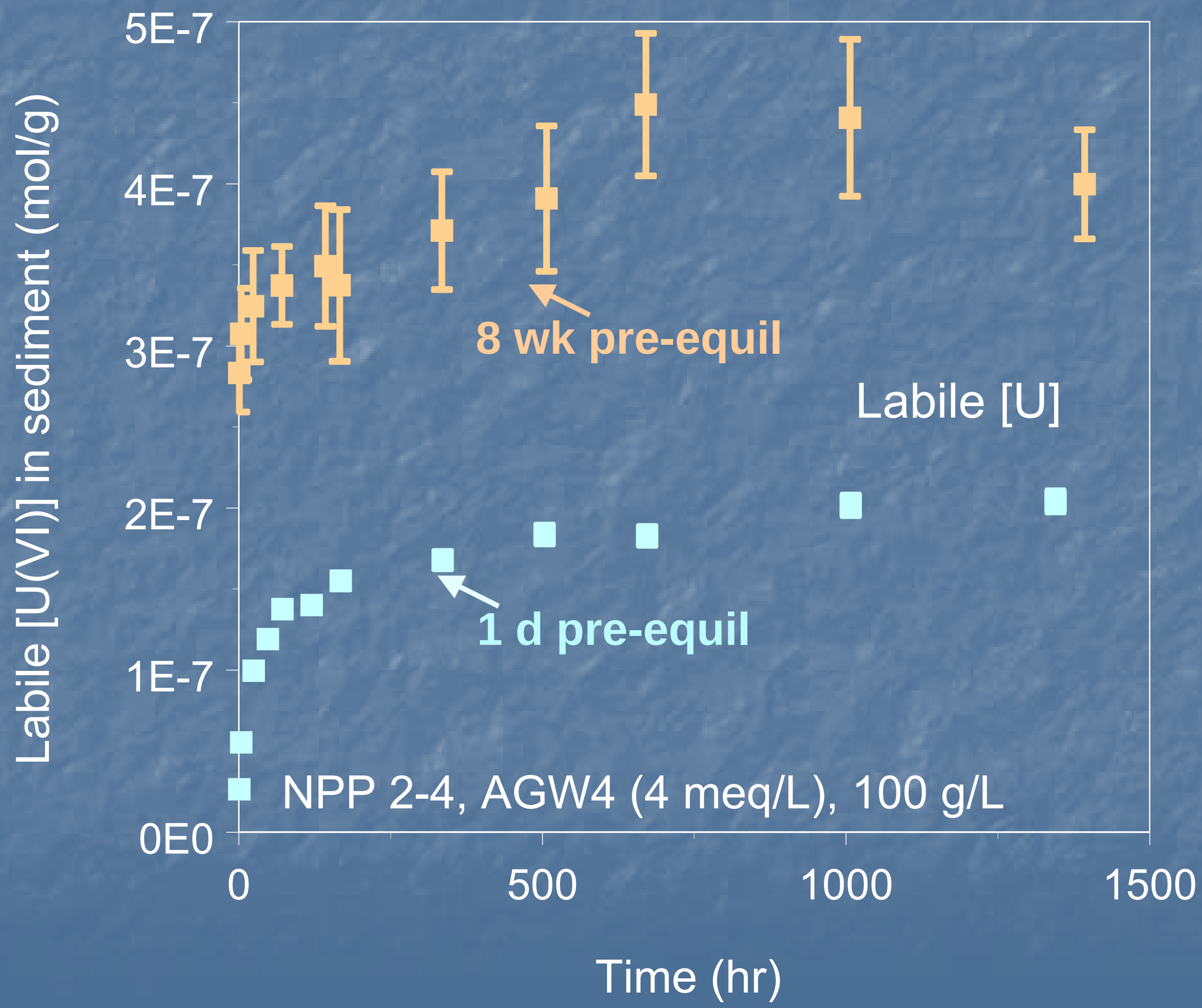
- Batch tracer experiments to complement column work
- Additional (high resolution) tracers
  - Better models for U(VI) species?
- Modeling of batch U(VI) data
  - "Kinetic" SCM (diffusion + surface complexation)

Porosity and Surface Area (N_2, Hg)

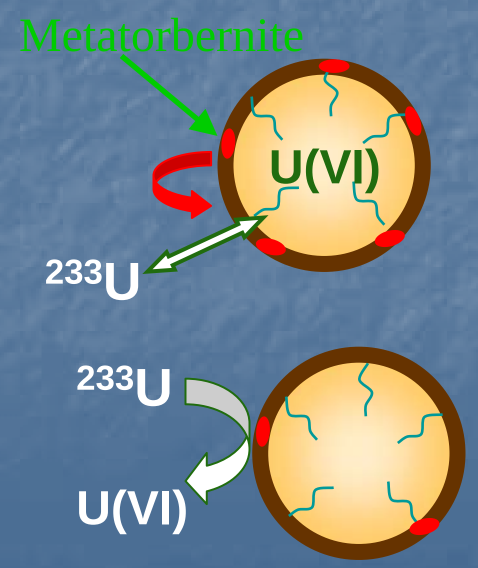
		Surface area (m^2/g)				Volume (cm^3/g)			
Pore diameter:		< 300 nm	< 100 nm	< 10 nm		< 300 nm	< 100 nm	< 10 nm	
NPP1-16	N_2	29.92				0.0892			
	Hg	12.33	12.07	6.94	56%	0.0615	0.0495	0.0096	16%
NPP1-20	N_2	17.44				0.0369			
	Hg	7.75	7.54	5.56	72%	0.0309	0.0214	0.0075	24%
SPP2-8	N_2	15.38				0.0339			
	Hg	7.52	7.33	5.08	68%	0.0316	0.0237	0.0077	24%

- Small volume in narrow pores, but <u>large</u> surface area
- Intragranular pore volume, while small, is highly reactive

^{233}U Exchange with 300-A Sediments



U(VI) concentration increases slowly
→ labile U(VI) calculation depends on pre-equilibration time
→ indicative of dissolution process



Chemical Extraction of Sediment Samples

Desorb U(VI) due to higher pH and carbonate complexation

Determine labile fraction of total sediment U(VI); adsorption-desorption; dissolution-reprecipitation

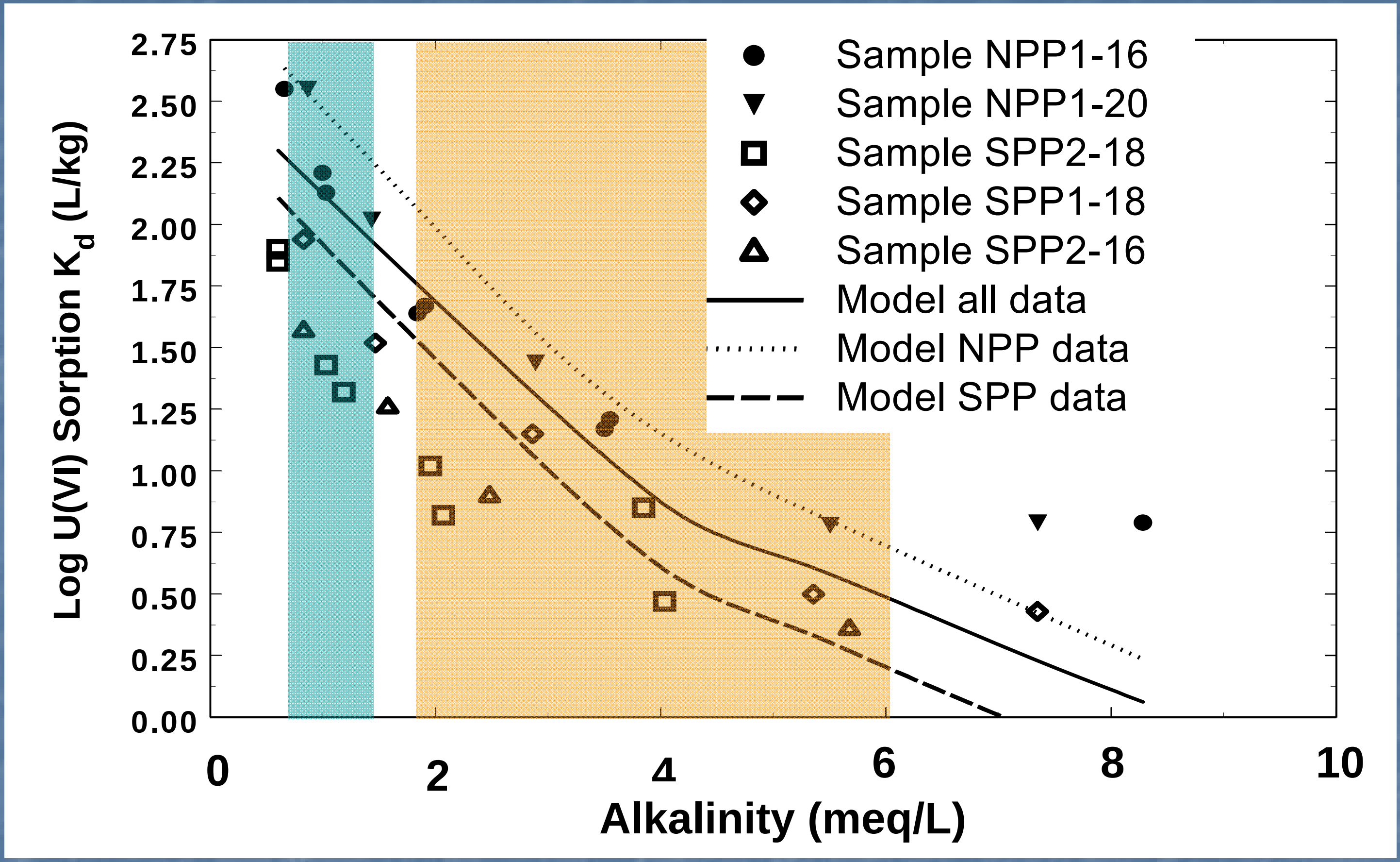
Desorb and dissolve U(VI) due to buffered, lower pH

Sample	Bicarbonate Extraction % of U_{tot}	Isotopic Exchange % of U_{tot}	Formate Extraction % of U_{tot}	Formate Extraction % of Cu_{tot}
SPP 1-18	36 ± 1	36 ± 1	79 ± 3	4 ± 0.1
SPP 2-16	42 ± 4	41 ± 2	93 ± 3	3 ± 0.1
NPP 1-20	30 ± 0.5	36 ± 1	**78 ± 3**	**14 ± 1**
NPP 2-4	29 ± 1	88 ± 9	**80 ± 2**	**91 ± 5**

Low pH dissolves most of Cu_{tot}; likely dissolves most of metatorbernite; deep samples don't have metatorbernite

Low pH releases large fraction of U_{tot}; dissolution of grain coatings releases co-precipitated U(VI) that is not "labile"?

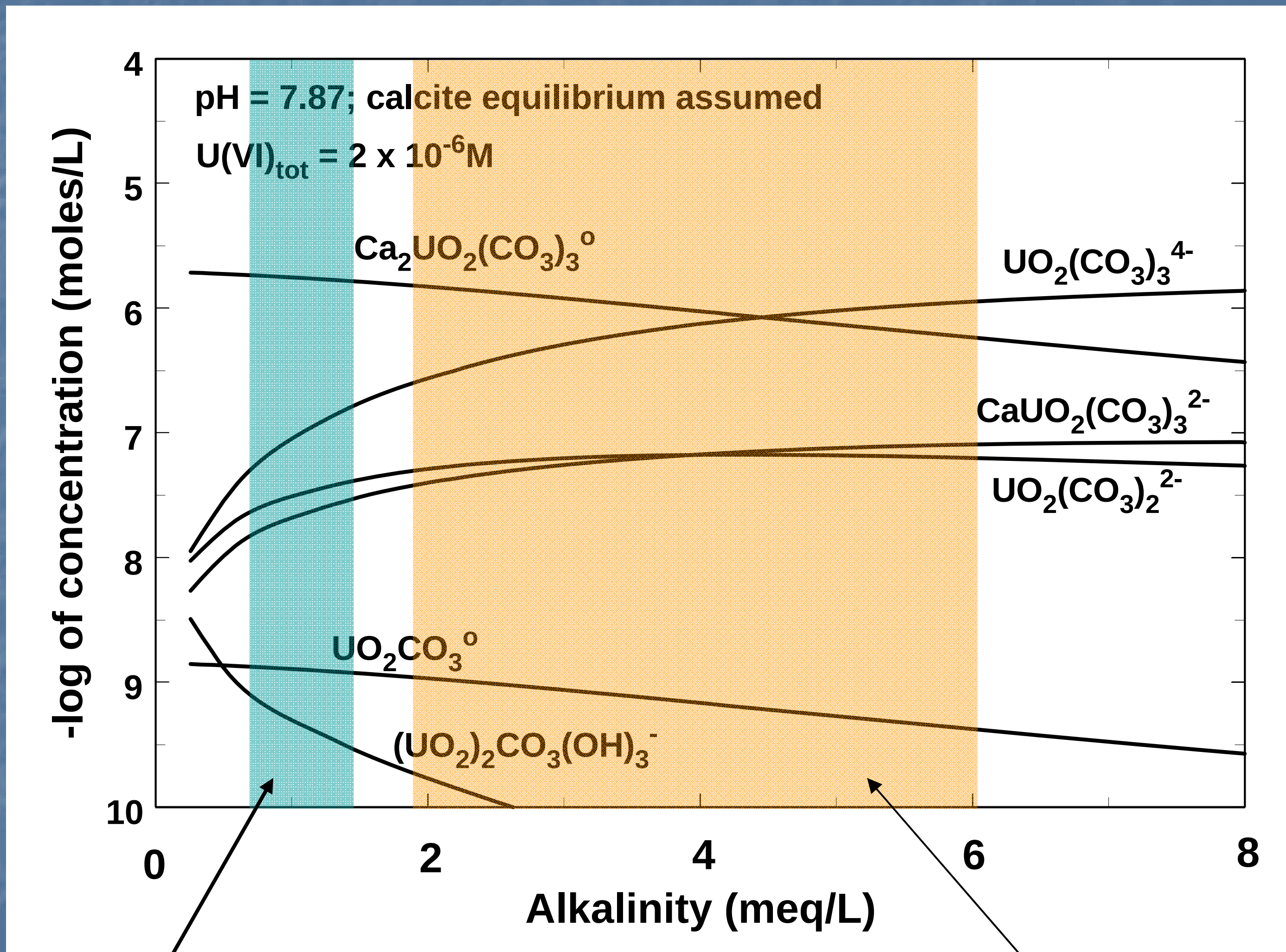
Surface Complexation Model



$$>SOH + UO_2^{2+} + H_2O = >SOUO_2OH + 2H^+ \quad \log K_1$$

$$>SOH + UO_2^{2+} + H_2CO_3 = >SOUO_2CO_3 + 2H^+ \quad \log K_2$$

Dissolved U(VI) Complexation

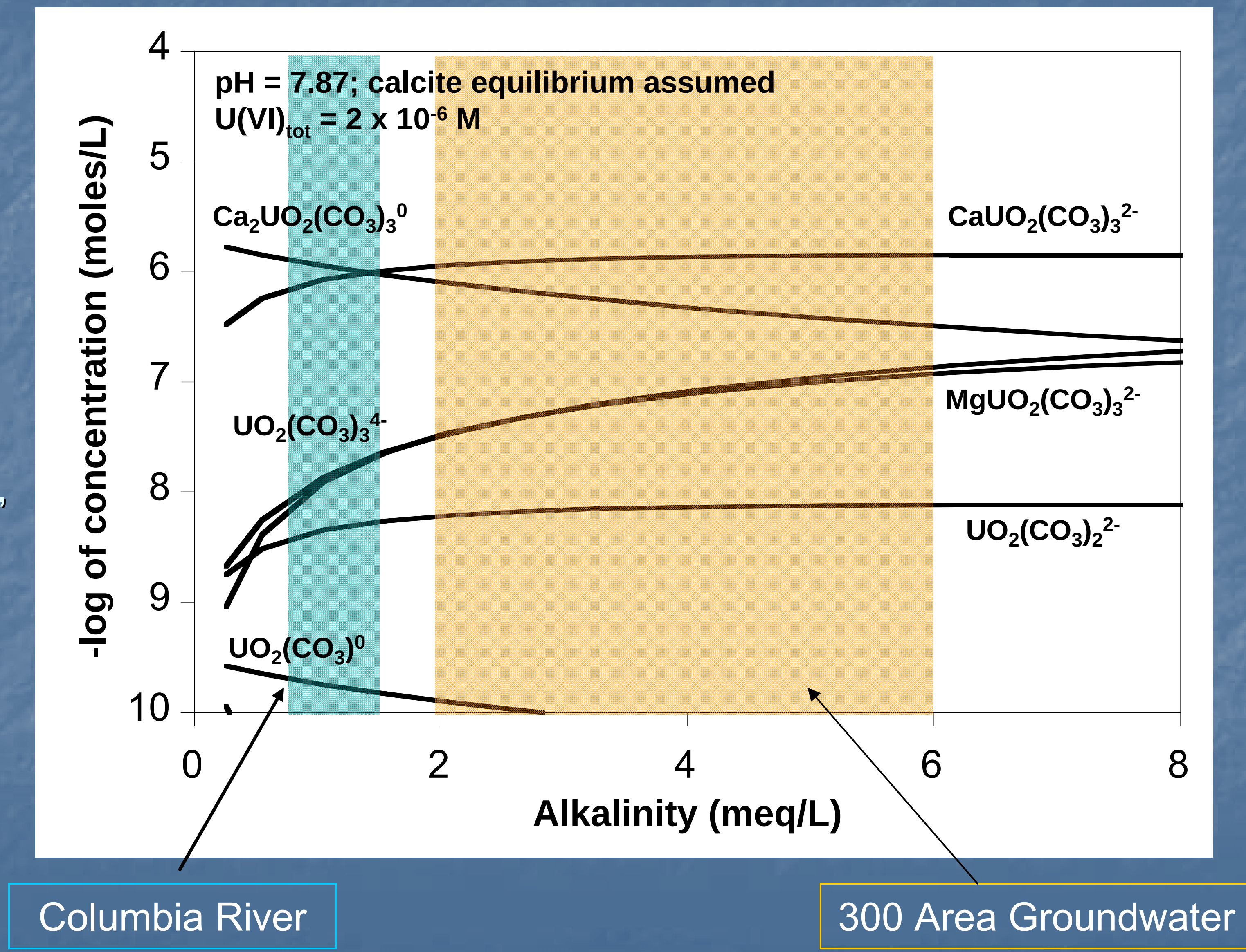


Columbia River

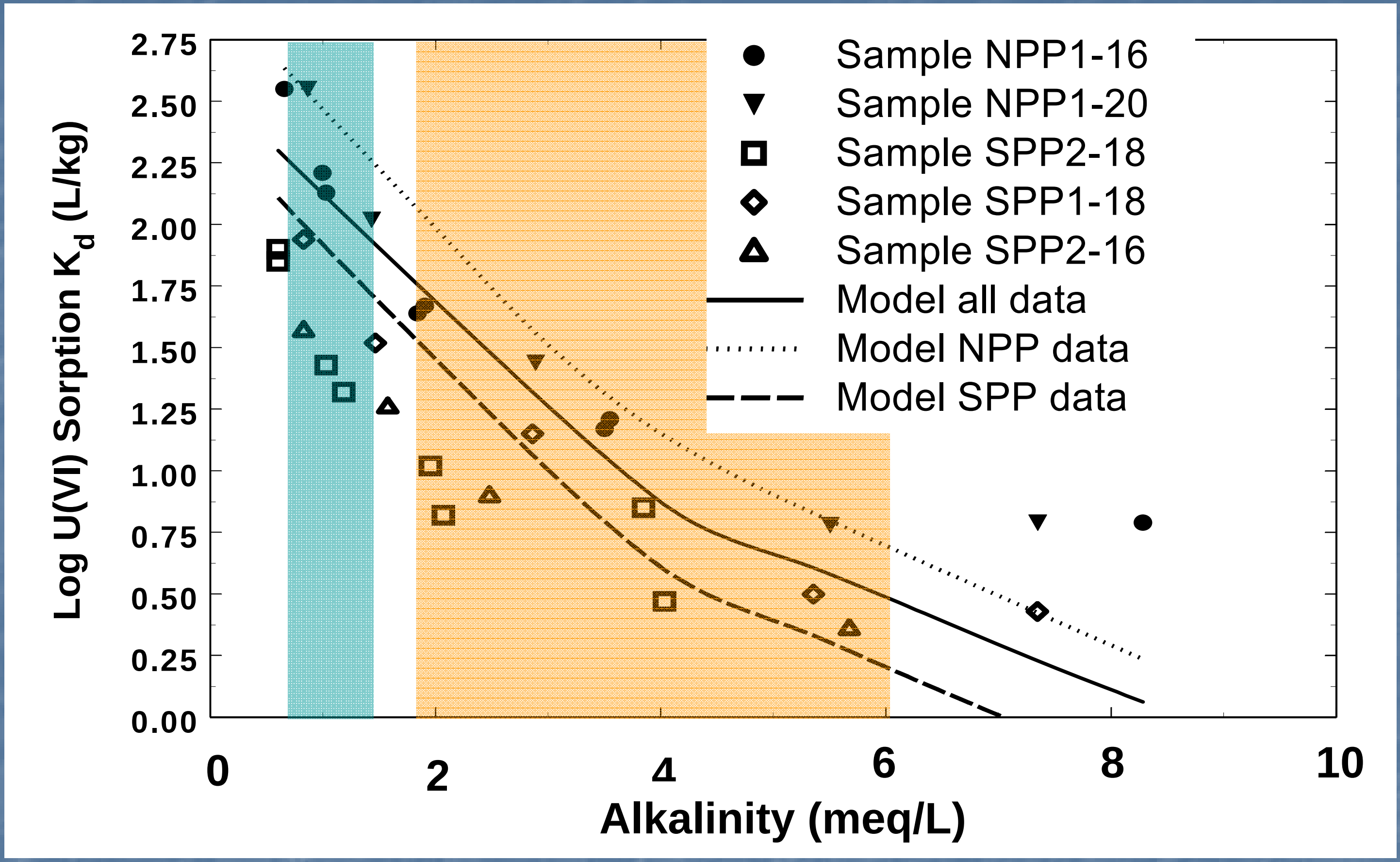
300 Area Groundwater

Updated Dissolved U(VI) Complexation

Dong and Brooks, 2006



Surface Complexation Model



$>SOH + UO_2^{2+} + H_2O \;=\; >SOUO_2OH + 2H^+ \qquad \log K_1$

$>SOH + UO_2^{2+} + H_2CO_3 \;=\; >SOUO_2CO_3 + 2H^+ \qquad \log K_2$

Magnified Particle Scale Showing Intraparticle Pore