Geochemical and Mass Transfer Processes in 300 A Sediments

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(PNNL-SA-54329)

EM-30 and ERSP

March 21-22, 2007

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Simple Conceptual Models for Geochemical Reaction of UO_2^{2+}

Aqueous Complexation

Hydrolysis $UO_{2(aq)}^{2+} + H_2O(1\text{-}4) = UO_2OH^{+}_{(aq)} + H^+$

Carbonate complexation $UO_{2(aq)}^{2+} + 3CO_3^{2-} = UO_2(CO_3)_{3(aq)}^{4-}$

and many others

Adsorption/Surface Complexation

$SOH_{(s)} + UO_2OH^{+}_{(aq)} = SO\ UO_2OH_{(s)} + H^+$

$2SOH_{(s)} + UO_2(CO_3)_{3(aq)}^{4-} + 2H^+ = (SOH_2^{+})_2UO_2(CO_3)_{(s)}^{2-}$

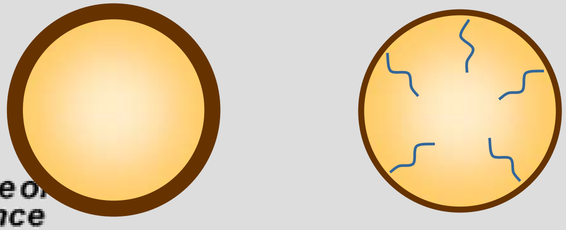
where SOH = SiOH, FeOH, AlOH

Precipitation

$2UO_{2(aq)}^{2+} + 2PO_{4(aq)}^{3-} + Cu_{(aq)}^{2+} + 6H_2O = Cu[(UO_2)(PO_4)]_2(H_2O)$

$UO_{2(aq)}^{2+} + Ca_{(aq)}^{2+} + 2CO_{3(aq)}^{2-} + 5H_2O = Ca[UO_2(CO_3)_2](H_2O)_{5(s)}$

Physical Considerations



The K_d

$$K_d = \frac{\Sigma\,[s]}{\Sigma\,[aq]}$$

Liability and Exchangeability of Sorbed U(VI) in 300 A Sediments

Sample	Total U (ppm) [a]	Formate Extraction % of U_{tot} [b]	Bicarbonate Extraction % of U_{tot} [c]	Isotopic Exchange % of U_{tot} [d]	Estimate of Adsorbed U(VI) % of U_{tot} [e]
NPP 1-8	10.5	101.5 ± 3.2	45.0 ± 0.2	46.0 ± 3.3	54
NPP 1-12	14.0	90.3 ± 3.1	42.7 ± 1.0	44.7 ± 3.6	61
NPP 1-16	9.6	82.5 ± 2.7	38.3 ± 3.3	44.6 ± 1.9	57
NPP 1-20	6.3	77.5 ± 2.5	29.7 ± 0.45	35.8 ± 0.70	41
NPP 2-2	105.7	72.5 ± 1.3	29.8 ± 2.8	46.4 ± 2.2	18
NPP 2-4	100.1	79.6 ± 1.6	29.4 ± 1.3	88.2 ± 8.6	13
NPP 2-8	39.8	68.3 ± 2.0	37.6 ± 1.1	56.3 ± 2.5	45
NPP 2-12	14.2	107.1 ± 1.2	56.1 ± 1.8	61.2 ± 2.0	70
SPP 1-16	7.3	101.9 ± 3.2	54.7 ± 0.99	55.1 ± 2.5	55
SPP 1-18	7.4	78.5 ± 2.5	36.0 ± 0.97	35.8 ± 0.74	28
SPP 1-22	7.9	68.9 ± 2.2	35.4 ± 0.08	37.1 ± 1.4	29
SPP 2-8	10.8	91.6 ± 2.9	43.8 ± 2.5	44.7 ± 4.9	52
SPP 2-12	8.0	100.1 ± 3.3	57.6 ± 1.2	54.7 ± 2.7	61
SPP 2-16	3.8	93.1 ± 2.8	41.0 ± 1.9	42.2 ± 4.0	34
SPP 2-18	2.9	61.0 ± 1.9	18.9 ± 1.3	21.1 ± 0.3	15
NPP 1-Fines	21.2	78.3 ± 0.89	41.4 ± 0.77	47.7 ± 2.1	57
NPP 2-Fines	157.1	--	41.4 ± 1.5	--	--
SPP 1-Fines	31.3	78.7 ± 0.89	58.0 ± 0.13	56.1 ± 7.0	66
SPP 2-Fines	13.3	75.8 ± 2.6	39.9 ± 0.68	52.6 ± 1.0	38

[*] Values are the mean of two replicates, error based on replicate variation.

[a] Sum of ^{238}U and ^{235}U (Uranium concentration in nmoles/g are listed in Table 4)

[b] Formate extraction (72 hr)

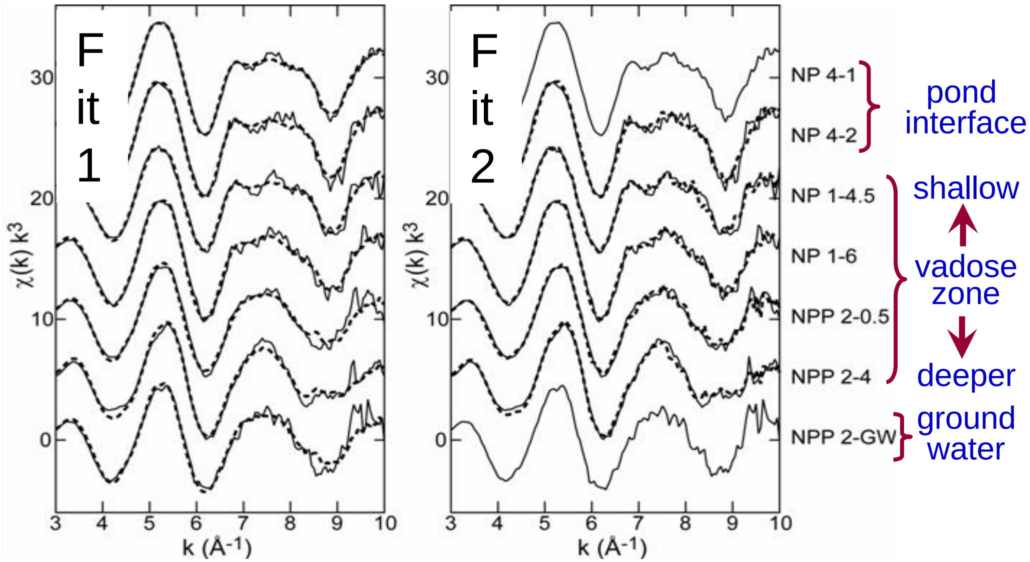
[c] Bicarbonate extraction, pH 9.45 (72 hr)

[d] Isotopic exchange, 336 hr (after 1260 hr pre-equilibration in AGW4).

[e] Estimate of adsorbed U(VI) in each sample from the semi-mechanistic surface complexation model calibrated with deep vadose zone samples. Adsorbed U(VI) in the sample calculated with the model by estimation of dissolved U(VI) concentration that would result from desorption after 96 hr equilibration in AGW4 (see text).

Depth Dependent Speciation Measurements and Resulting Model

Two Fit Models were Applied to the EXAFS Data



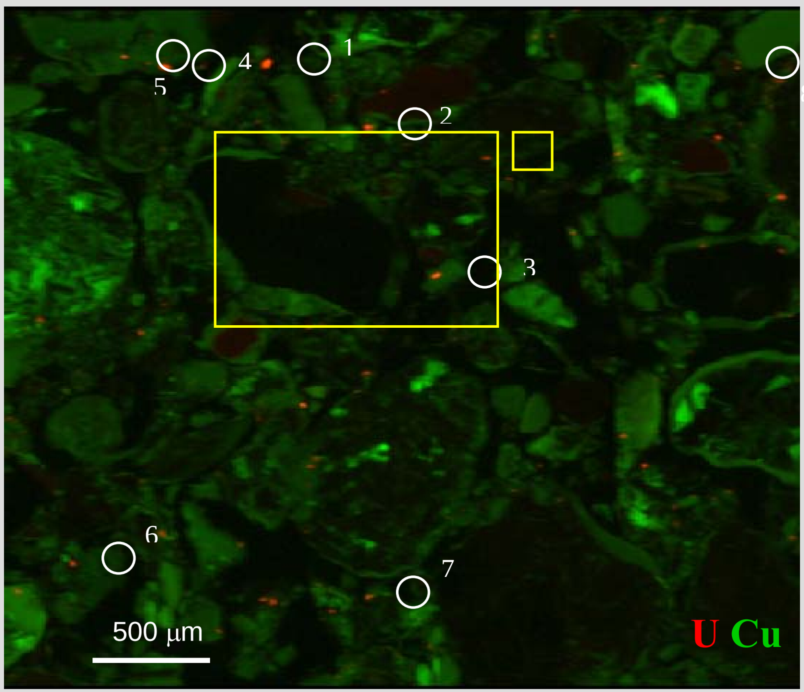
Results of Linear Combination Fitting

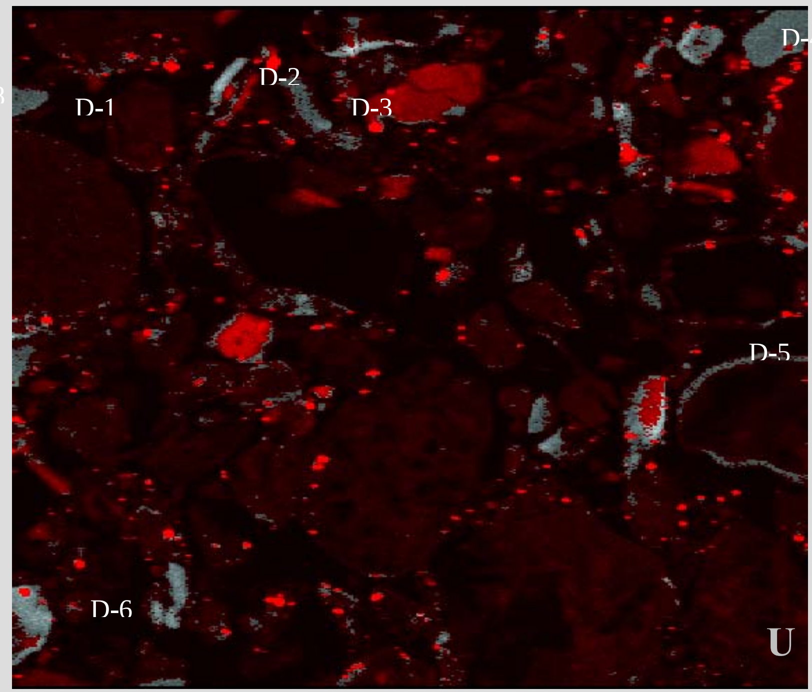
Fit 1	NP 4-1	NP 4-2	NP 1-4.5	NP 1-6	NPP 2-0.5	NPP 2-4	NPP 2-GW
Liebigite	0.49(2)[a]	0.52(4)	0.45(4)	0.34(4)	0.00(5)	0.00(4)	0.02(6)
U(VI)-sorbed montmorillonite	0.42(4)	0.42(6)	0.37(6)	0.54(6)	0.84(8)	0.54(6)	0.87(9)
Metatorbernite	0.03(2)	0.00(4)	0.00(4)	0.11(4)	0.05(5)	0.41(4)	0.00(6)
Component Sum[b]	0.92	0.94	0.83	0.98	0.89	0.95	0.89
χ^{2} [c]	0.05	0.16	0.17	0.18	0.28	0.18	0.42

Fit 2	NP 4-1	NP 4-2	NP 1-4.5	NP 1-6	NPP 2-0.5	NPP 2-4	NPP 2-GW
NP 4-1	1	1.00(5)	0.98(4)	0.75(4)	0.16(4)	0.02(4)	0
NPP 2-GW	0	0.03(6)	0.00(5)	0.17(5)	0.63(5)	0.43(5)	1
Metatorbernite	0	0.00(3)	0.00(2)	0.15(2)	0.22(2)	0.55(2)	0
Component Sum	1	1.03	0.98	1.07	1.00	1.00	1
χ^2	N/A	0.23	0.15	0.16	0.16	0.15	N/A

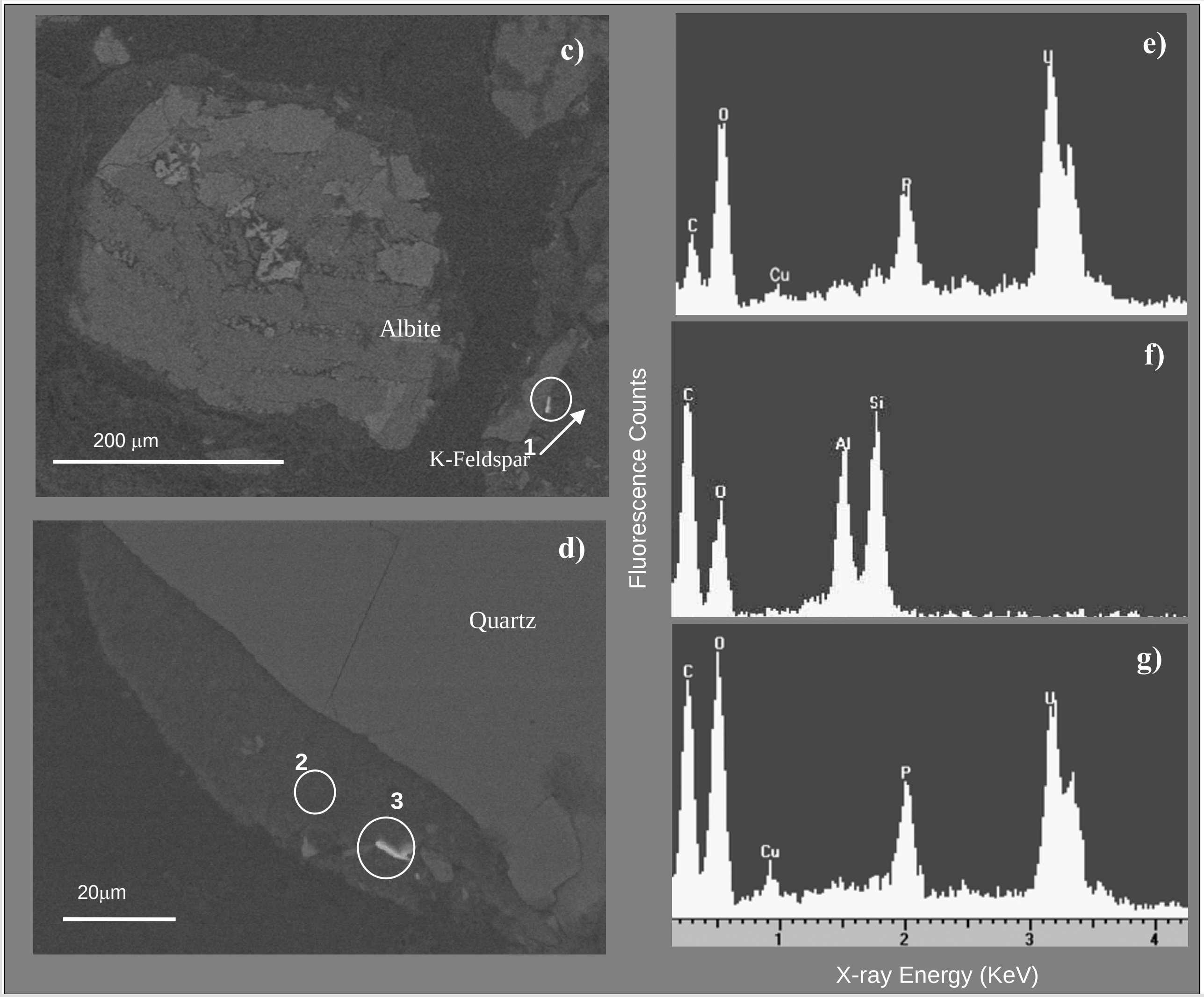
[a]Estimated standard deviations of the final digit are shown in parentheses.
[b]Sum of fractional fit components.
[c]Chi-squared, a goodness-of-fit parameter.

Synchrotron X-Ray Microprobe Measurements of Sorbed U(VI) in Vadose Zone Sediment NPP2-4

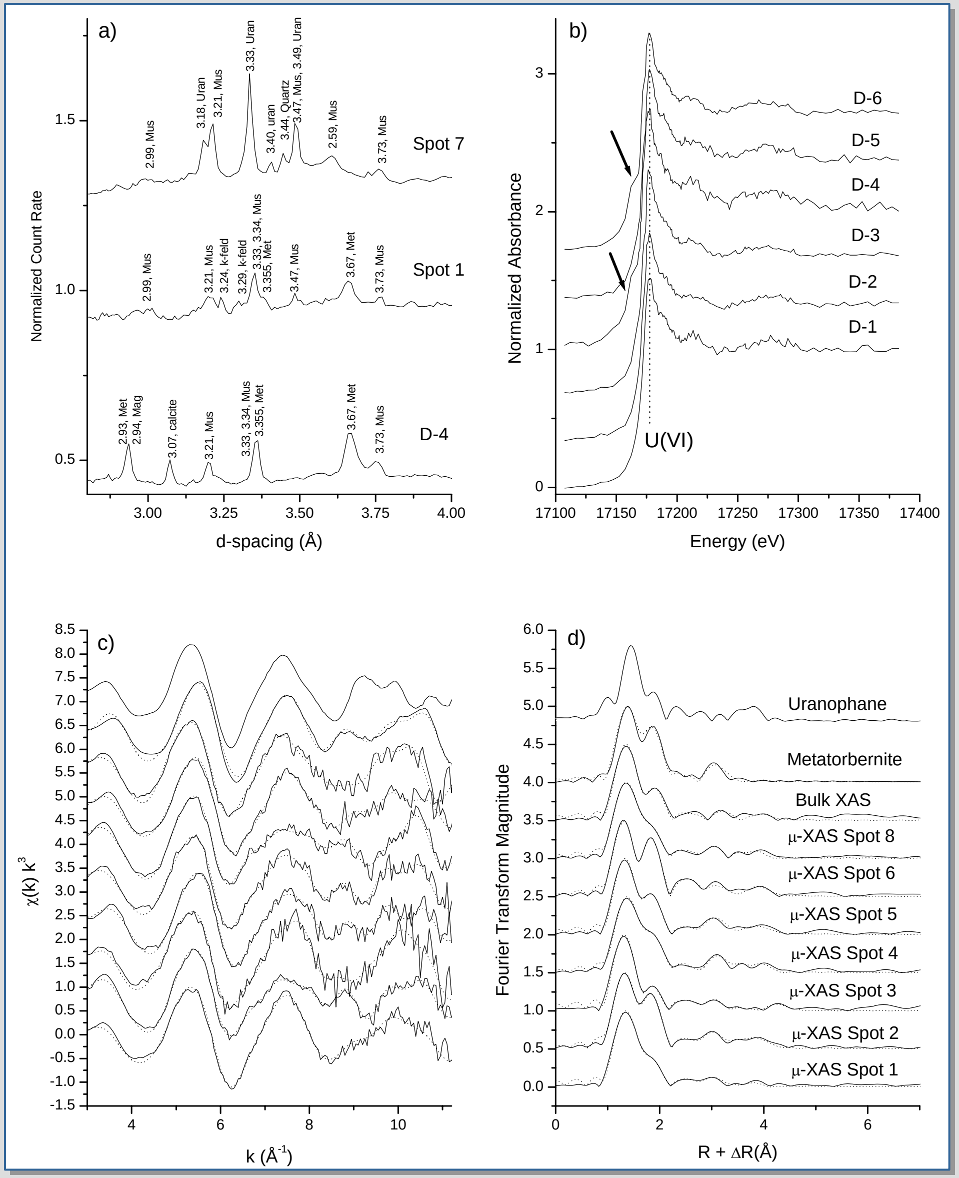




TEM and EDS on NPP2-4 Thin Section Identifies Grain Coatings with Intra-Coating Precipitates



Synchrotron Measurements on NPP2-4



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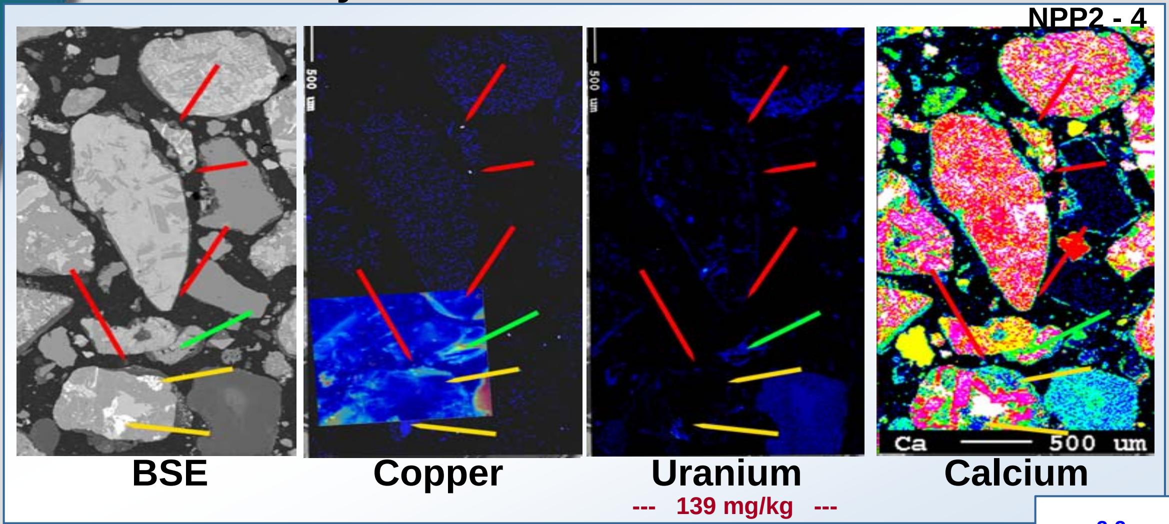
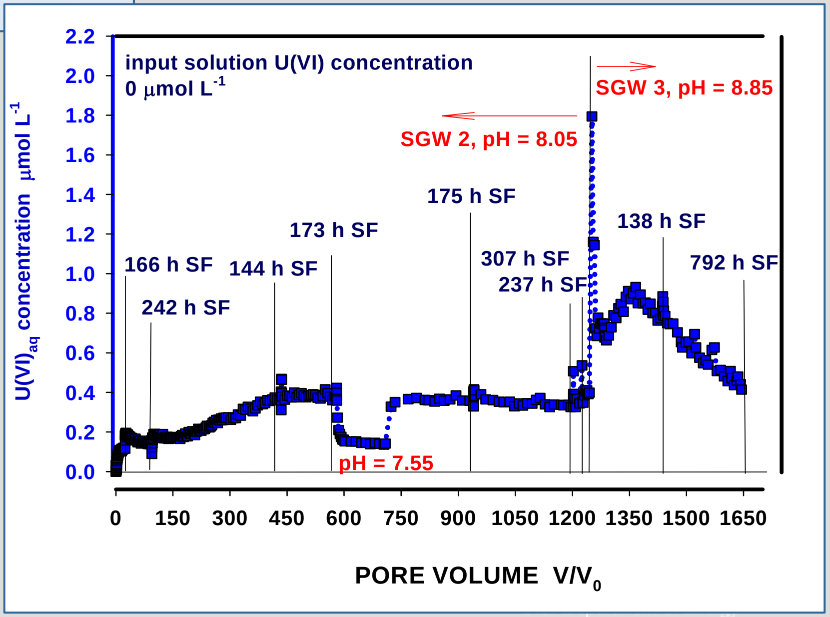
Solubility-Controlled Release of Sorbed U(VI) from Vadose Zone Sediment NPP2-4

BSE-XRF Overlay



Column Dissolution Behavior



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The Distribution Ratio and Solid Phase Properties

	U(VI) K_d (<2.0 mm)	Silt & Clay	SA	Extractable Fe(III) HAHCl	AmOx	DCB
	(mL/g)	(mass %)	(m^2/g)	(μmol/g)		
SPP2-18' bgs	9.23±5.87	7	14.3	19	48	77
NPP2-16' bgs	82.5±48.3	30	23.6	41	91	158

XRD Estimated Mineral Composition of Clay Fraction

	SPP2-18' bgs	NPP1-16' bgs
	(%)	(%)
Clinochlore	29	42
Muscovite	27	30
Montmorillonite	34	20
HIV	7	5
Feldspar & quartz	3	3

U(VI) Adsorption on 300 Area Sediments from Different Groundwaters

	Inorganic C (meq/L)	K_d (mL/g) 1-Day Contact SPP Pit 2 (18 ft bgs)		K_d (mL/g) 1-Day Contact NPP Pit 1 (16 ft bgs)		K_d (mL/g) 7-Day Contact SPP Pit 2 (18 ft bgs)		K_d (mL/g) 7-Day Contact NPP Pit 1 (16 ft bgs)	
GW 1	2.02	10.8	(0.02)	61.3	(0.12)	8.67	(0)	63.7	(0.26)
GW 2	1.70	13.2	(0.06)	83.2	(2.58)	9.51	(0.40)	85.6	(2.64)
GW 3	1.20	30.5	(3.97)	168	(7.08)	19.0	(1.76)	178	(7.38)
GW 4	2.41	11.3	(5.68)	33.9	(7.22)	14.6	(7.46)	37.8	(8.07)
GW 5	1.58	2.28	(0)	82.6	(12.8)	3.31	(0.30)	89.7	(13.6)
GW 6	2.47	2.22	(1.32)	30.5	(14.5)	2.82	(1.77)	33.5	(15.7)
GW 7	1.70	ND	ND	85.7	(17.5)	6.76	(1.96)	89.3	(17.7)

GW 1 = NPP pit 1 groundwater (58154-139); 71.4 ppb U; pH 8.29
GW 2 = SPP pit 2 groundwater (58154-132); 84.8 ppb U; pH 8.28
GW 3 = SPP pit 1 groundwater (58154-133); 70.7 ppb U; pH 8.12
GW 4 = 618-5 pit 2 groundwater; sampled 2-26-03 (58154-97-3); 433 ppb U; pH 8.43
GW 5 = NPP pit 2 groundwater (58155-17); 247.3 ppb U; pH 8.22
GW 6 = 618-5 pit 1 groundwater; sampled 2-26-03 (58154-97-4); 1181 ppb U; pH 8.30
GW 7 = SPP pit 2 groundwater spiked to ~250 ppb U; 324 or 269 ppb U; pH 8.29 or 8.08

( ) = The labile U is not considered.

K_d Estimation for "*In-Situ*" 300 Area Sediments

Basic Data

SPP2-18', K_d (< 2.0 mm) = 9.24 ± 5.87 mL/g

NPP1-16', K_d (< 2.0 mm) = 82.5 ± 48.3 mL/g

F = .917 (> 2.0 mm)

I-F = .083 (< 2.0 mm)

K_d Estimation [*Cantrell, Serne, and Last (2002)*]

K_{dgc} = (I-F) K_d < 2.0 mm + (F) 0.23 K_d < 2.0 mm

SPP2-18', $K_{d(gc)}$ = 1.94 (0.73 – 4.43)

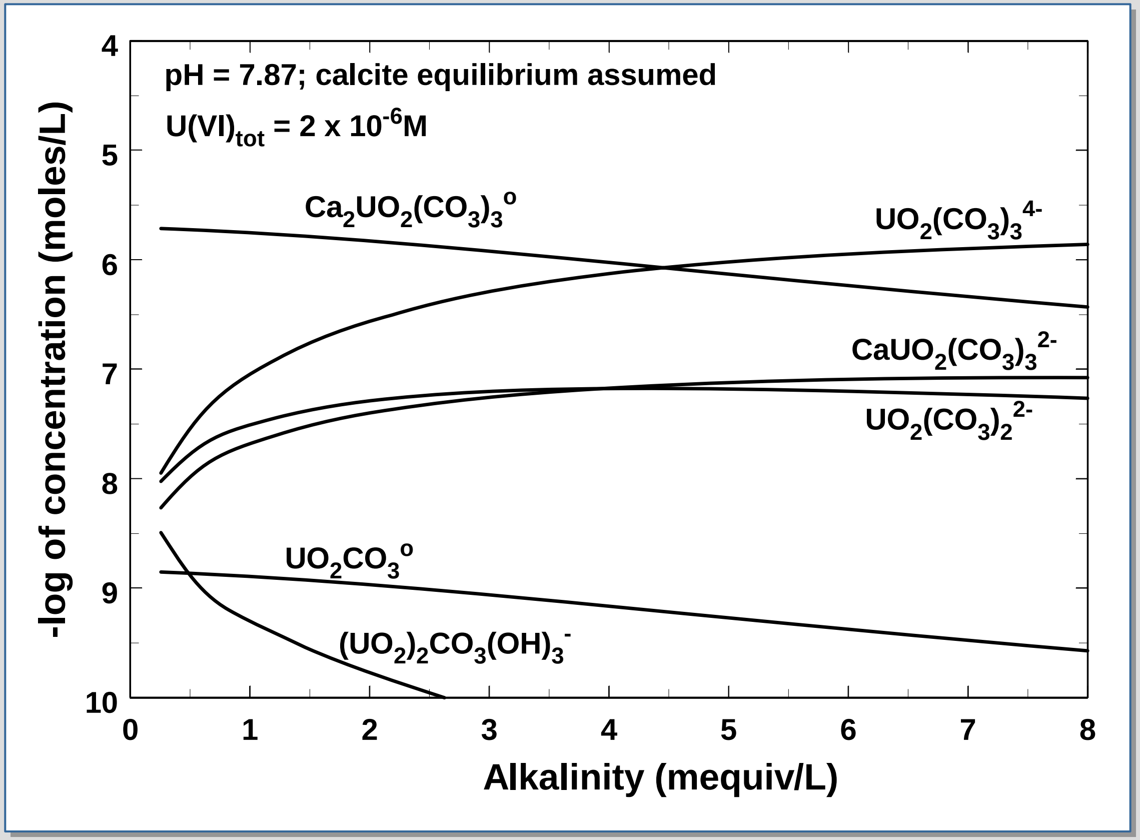
NPP1-16', $K_{d(gc)}$ = 24.2 (10.1 – 38.4)

K_{dgc} = (I-F) K_d < 2.0 mm

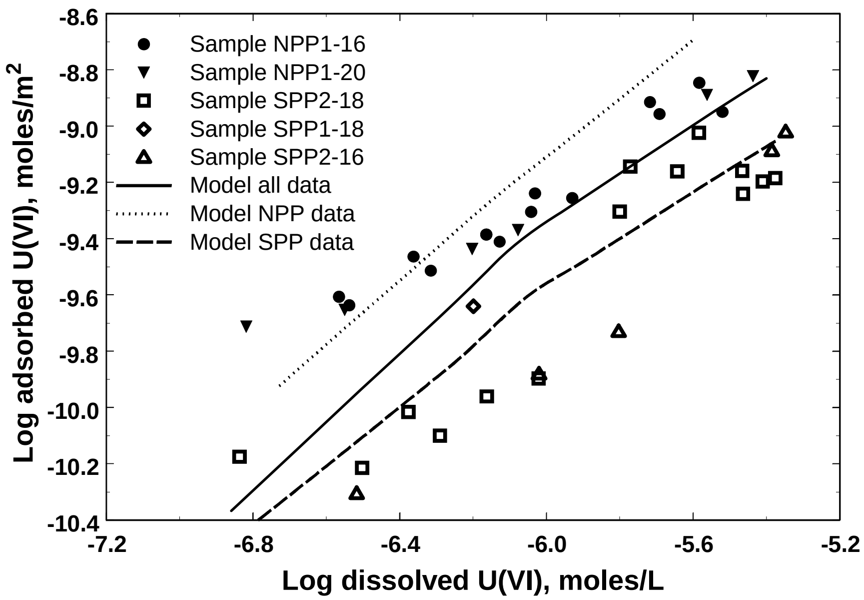
SPP2-18', $K_{d(gc)}$ = 0.76 (0.27 – 1.25)

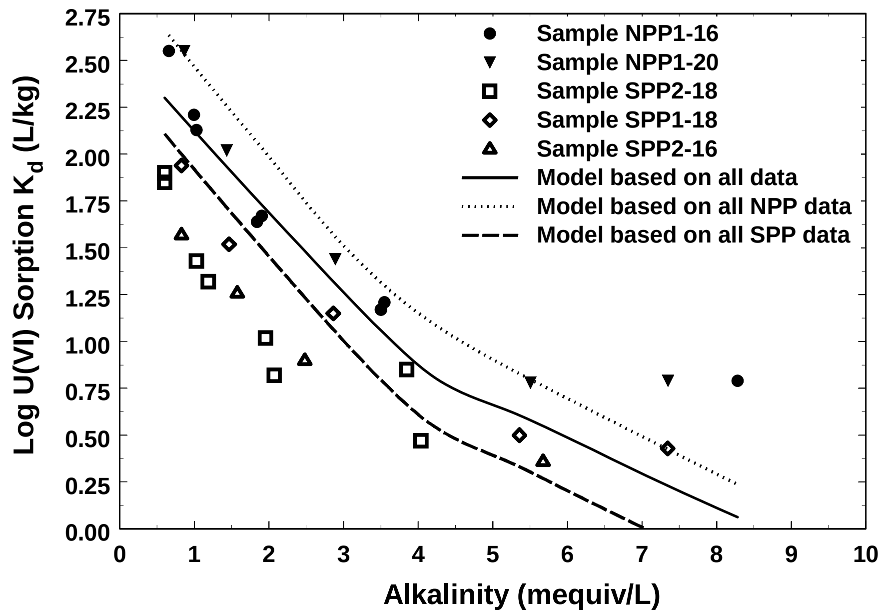
NPP1-16', $K_{d(gc)}$ = 6.84 (2.84 – 10.85)

Dependence of U(VI) Speciation on Alkalinity (HCO_3^- + CO_3^{2-})



Surface Complexation Modeling of U(VI) Desorption from 300 A Sediments





Surface Complexation Model Parameters

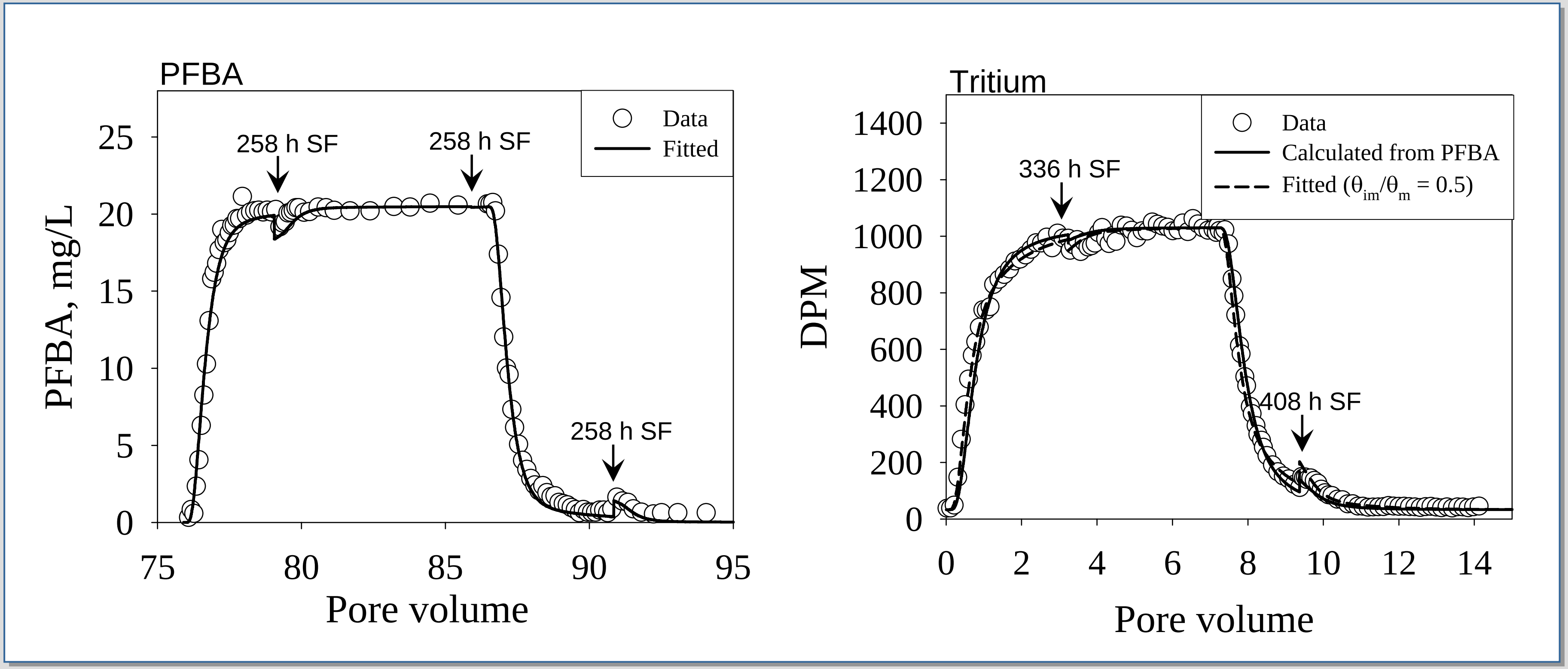
U(VI) Surface Reaction	Log K_f (I=0)
Average Model based on all data	
$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$	-5.152
$SOH + UO_2^{2+} + H_2CO_3 = SOHUO_2CO_3 + 2H^+$	-0.833
NPP Sediment Model	
$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$	-4.722
$SOH + UO_2^{2+} + H_2CO_3 = SOHUO_2CO_3 + 2H^+$	-0.895
SPP Sediment Model	
$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$	-5.235
$SOH + UO_2^{2+} + H_2CO_3 = SOHUO_2CO_3 + 2H^+$	-1.033

Large Column Experiment with NPP1-14 to Investigate Scaling Issues

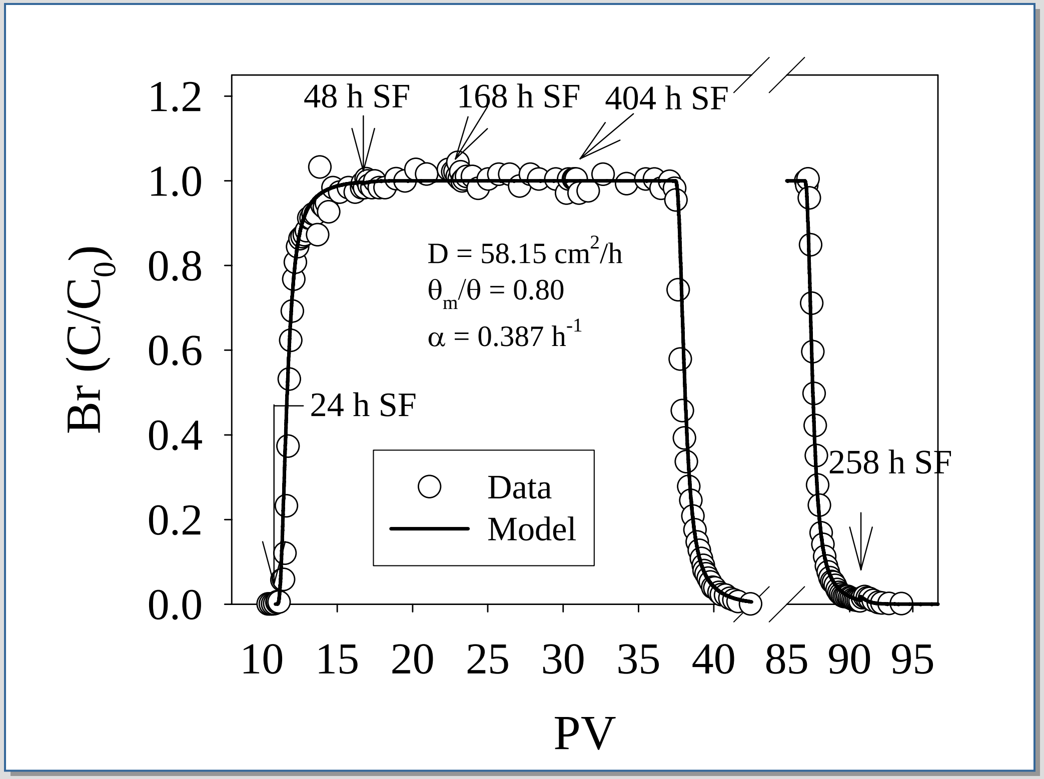
Unseived Sediment with River Cobble and Mud

The 80 kg Column

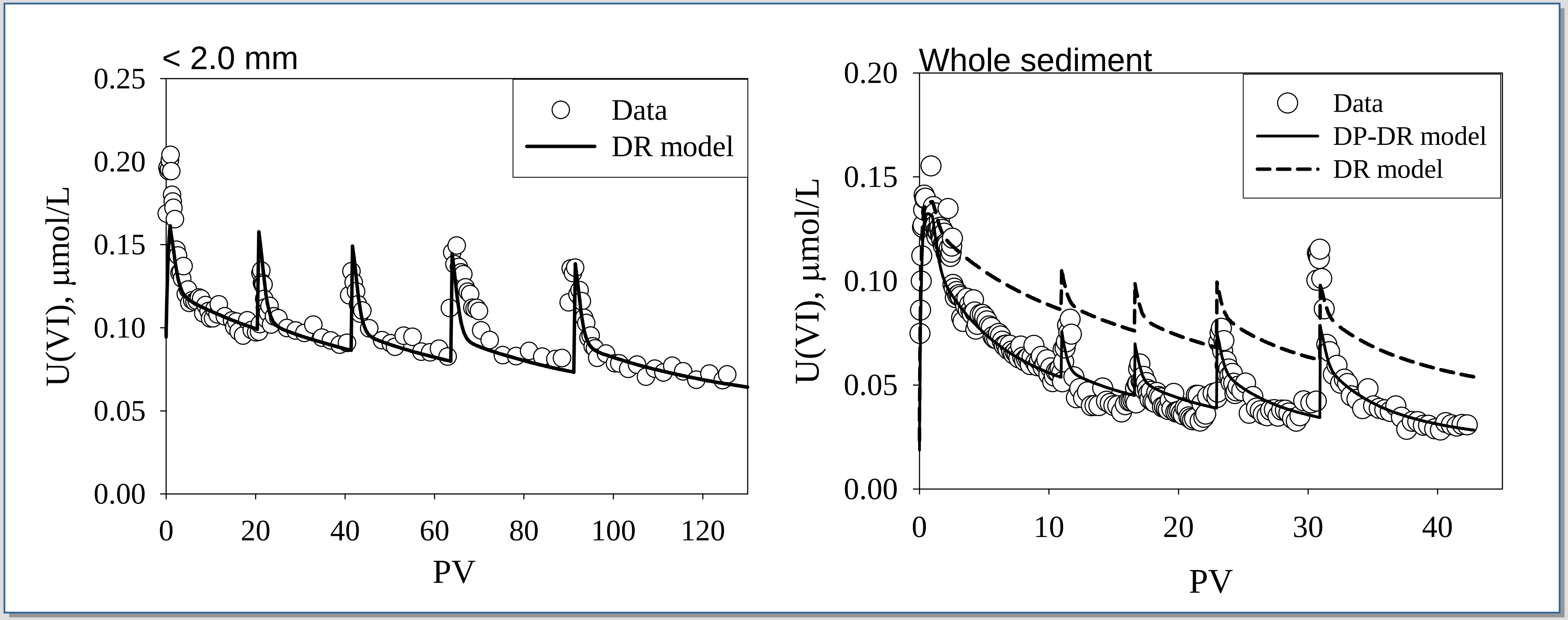
Tracer Breakthrough in Large Columns of NPP 1-14 and Two-Region Model Fitting



Modeling Br⁻ Transport in Large Column with Parameters Derived from PFBA



Modeling U(VI) Desorption from 300 A Sediments with the Distributed Rate (DR) and Dual Porosity – Distributed Rate (DP-DR) Models



Mass Transport Equations

Transport Equation:

$$\theta \frac{\partial C_i^m}{\partial t} + (1-\theta)\rho_s \frac{\partial q_i^m}{\partial t} + \theta_{im} \frac{\partial C_i^{im}}{\partial t} + (1-\theta_{im})\rho_s \frac{\partial q_i^{im}}{\partial t} = \theta AD(C_i^m)$$

i =1, 2, …, N

Mobile Domain Multi-Rate Equation:

$$\frac{\partial q_i^m}{\partial t} = \sum_{k=1}^{ME} \frac{\partial q_i^{m,k}}{\partial t} = \sum_{k=1}^{ME} \alpha_k^m (S_i^m - q_i^{m,k}) \qquad S_i^m = f(C_{1,}^m C_2^m, \ldots, C_N^m)$$

Mass Exchange Between Mobile and Immobile Domains:

$$\theta_{im} \frac{\partial C_i^{im}}{\partial t} + (1-\theta_{im})\rho_s \frac{\partial q_i^{im}}{\partial t} = \theta_{im}\alpha_{im}(C_i^m - C_i^{im})$$

Immobile Domain Multi-Rate Equation:

$$\frac{\partial q_i^{im}}{\partial t} = \sum_{k=1}^{ME} \frac{\partial q_i^{im,k}}{\partial t} = \sum_{k=1}^{ME} \alpha_k^{im} (S_i^{im} - q_i^{im,k}) \qquad S_i^{im} = f(C_{1,}^{im} C_2^{im}, \ldots, C_N^{im})$$

C_i^m and q_i^m: aqueous and sorbed component i in mobile domain; C_i^{im} and q_i^{im}: aqueous and sorbed component i in immobile domain; $\mathrm{q_i^{m,k}}$ and $\mathrm{q_i^{im,k}}$: sorbed component i on k^{th}-site in mobile and immobile domains, S_i^m and S_i^{im}: equilibrium concentrations of sorbed component i based on surface complexation reactions in the mobile and immobile domains

Surface Complexation Reactions Used in Modeling

Reactions	log K
$>SOH + UO_2^{2+} + H_2O = >SOUO_2OH + 2H^+$	-4.72
$>SOH + UO_2^{2+} + CO_3^{2-} = >SOUO_2HCO_3$	16.79

Conclusions

- Sorption degree dependent in groundwater composition and materials properties
  - DIC and Ca^{2+}
  - Silt and clay
  - Extractable Fe(III) ?
  - Clinochlore ?

- $K_{d(gc)}$ may range between 0.27-38.4 mL/g
  - F_g and F_{s+c} are critical
  - Large, undocumented spatial variance across 300 A

- Sorption and desorption reach a common equilibrium state
  - Significant times are required

- Mass transfer is slow
  - Proportional to sorption strength
  - Multiple rate and multiple domain behavior apparent

Formation Constants for U(VI) Solution Species

Reaction	log ß* (I = 0)[a]
$UO_2^{2+} + H_2O \Leftrightarrow UO_2OH^+ + H^+$	-5.25
$UO_2^{2+} + 2H_2O \Leftrightarrow UO_2(OH)_{2,aq} + 2H^+$	-12.15
$UO_2^{2+} + 3H_2O \Leftrightarrow UO_2(OH)_3^- + 3H^+$	-20.25
$UO_2^{2+} + 4H_2O \Leftrightarrow UO_2(OH)_4^{2-} + 4H^+$	-32.4
$2UO_2^{2+} + H_2O \Leftrightarrow (UO_2)_2OH^{3+} + H^+$	-2.70
$2UO_2^{2+} + 2H_2O \Leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H^+$	-5.62
$3UO_2^{2+} + 4H_2O \Leftrightarrow (UO_2)_3(OH)_4^{2+} + 4H^+$	-11.90
$3UO_2^{2+} + 5H_2O \Leftrightarrow (UO_2)_3(OH)_5^+ + 5H^+$	-15.55
$3UO_2^{2+} + 7H_2O \Leftrightarrow (UO_2)_3(OH)_7^- + 7H^+$	-32.20
$4UO_2^{2+} + 7H_2O \Leftrightarrow (UO_2)_4(OH)_7^+ + 7H^+$	-21.9
$UO_2^{2+} + CO_3^{2-} \Leftrightarrow UO_2CO_3(aq)$	9.94
$UO_2^{2+} + 2CO_3^{2-} \Leftrightarrow UO_2(CO_3)_2^{2-}$	16.61
$UO_2^{2+} + 3CO_3^{2-} \Leftrightarrow UO_2(CO_3)_3^{4-}$	21.84
$2UO_2^{2+} + CO_3^{2-} + 3H_2O \Leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3H^+$	-0.855
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \Leftrightarrow CaUO_2(CO_3)_3^{2-}$	25.64 [b]
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \Leftrightarrow Ca_2UO_2(CO_3)_3$ (aq)	30.04 [c]
$UO_2^{2+} + NO_3^- \Leftrightarrow UO_2NO_3^+$	0.3
$UO_2^{2+} + Cl^- \Leftrightarrow UO_2Cl^+$	0.17
$UO_2^{2+} + 2Cl^- \Leftrightarrow UO_2Cl_2(aq)$	-1.1
$UO_2^{2+} + SO_4^{2-} \Leftrightarrow UO_2SO_4(aq)$	3.15
$UO_2^{2+} + 2SO_4^{2-} \Leftrightarrow UO_2(SO_4)_2^{2-}$	4.14

[a] Values from Guillaumont et al. (2003), unless otherwise indicated.

[b] Bernhard et al. (2001), with correction to be consistent with Guillaumont et al. (2003).

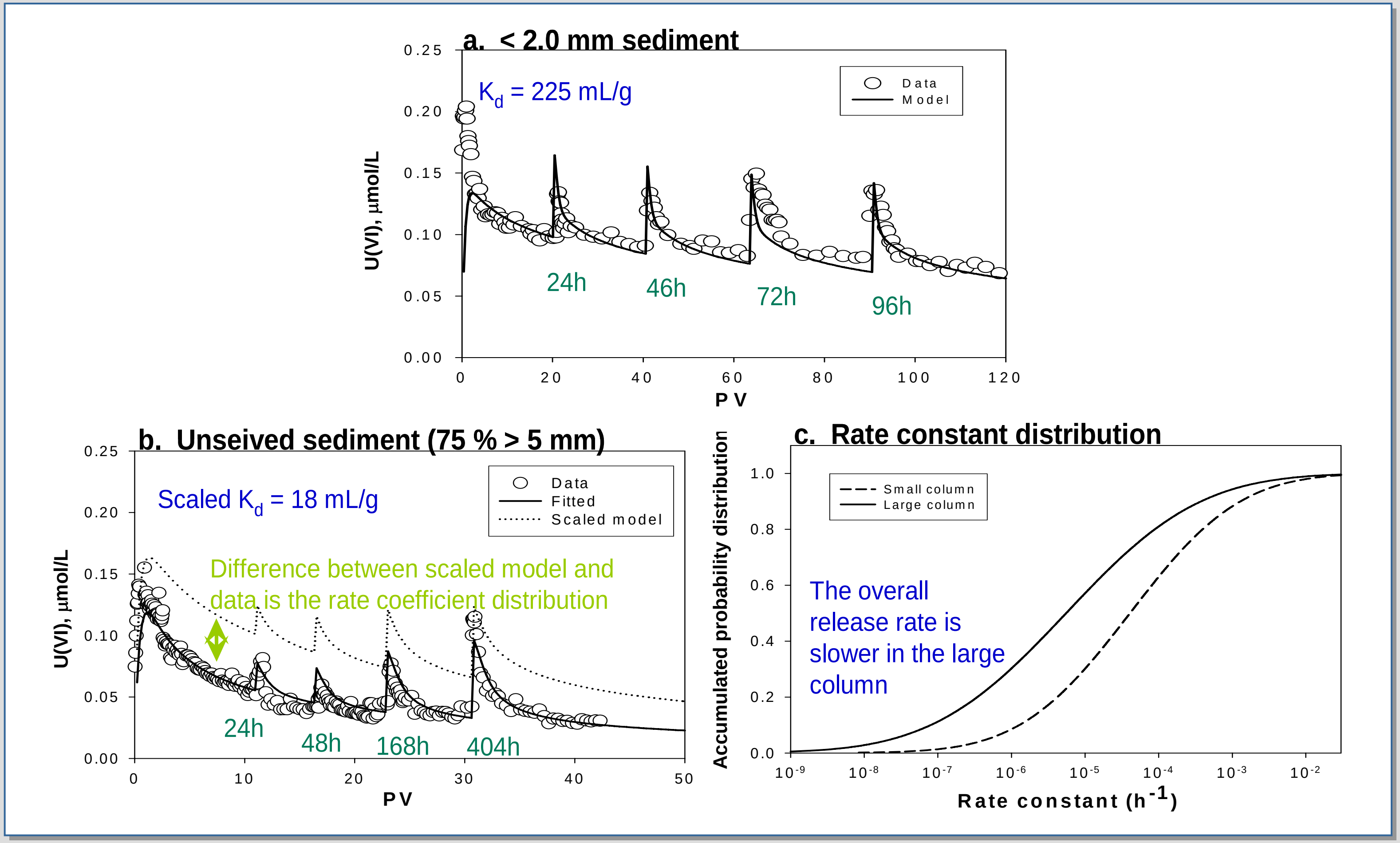
[c] Kalmykov and Choppin (2000), with correction to be consistent with Guillaumont et al. (2003).

Parameters in Modeling U(VI) Desorption

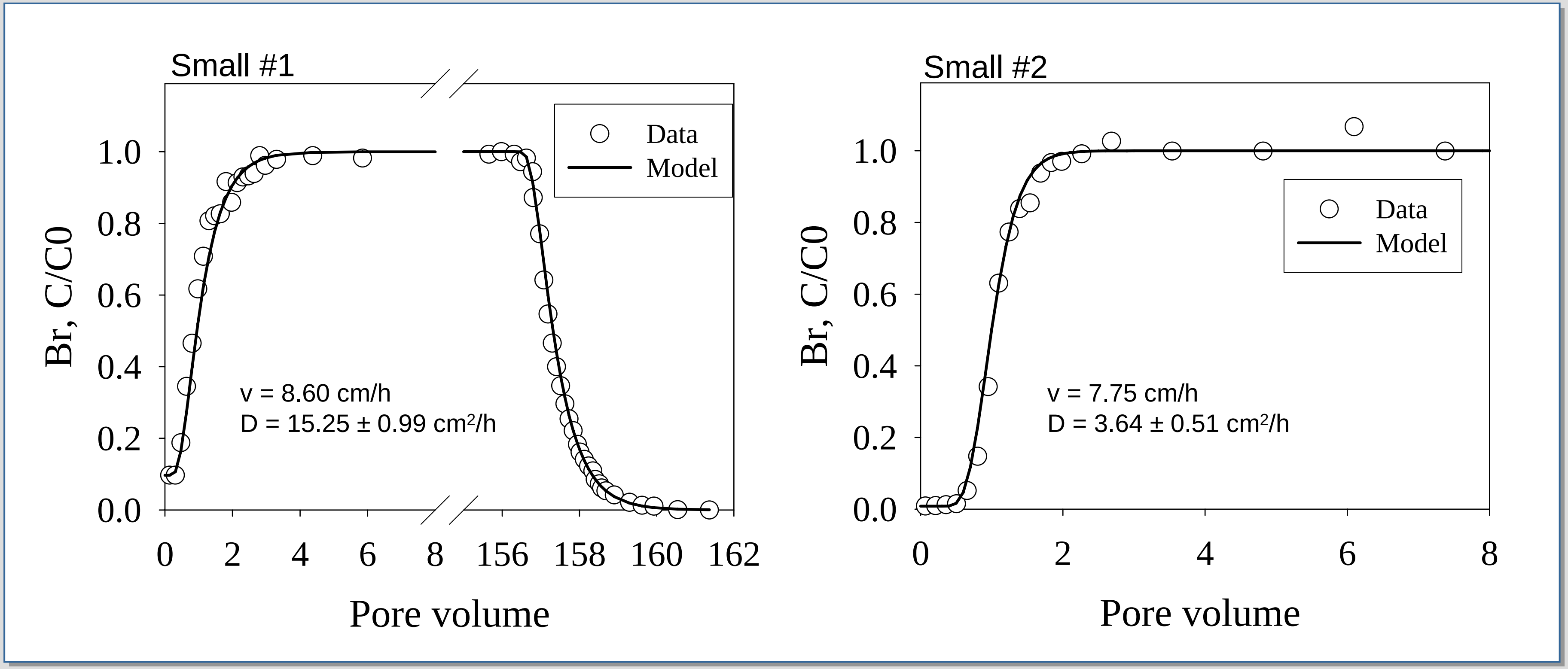
Parameters	Symbol	Unit	SC-1	SC2	LC
Column Length	L	cm	10.5	10.5	80
Pore velocity	v	cm/h	8.60	7.75	3.52
Dispersion coefficient	D	cm2/h	15.25	3.64	46.52
Porosity	θ	/	0.41	0.46	0.32
Soil bulk density	ρ_b	kg/L	1.56	1.42	1.88
Immobile porosity	θ_{im}	/	0.00	0.00	0.064
Logarithm mean rate	μ	log(h^{-1})	-9.99	-9.99	-9.99
Standard deviation	σ	log(h^{-1})	2.66	2.66	2.66

	PFBA	Tritium	Br	U(VI)
Two domain mass exchange rate constant (h^{-1})	1.45×10^{-2}	4.28×10^{-2}	3.87×10^{-2}	1.45×10^{-2}

Comparative Results of Large and Small Column Desorption Studies with NPP1-14



Non-Reactive Equilibrium Transport Behavior of Br^- in Small Columns of NPP 1-14



U(VI) Surface Reactions Considered for the Generalized Composite SCM

Number	Reaction
1	$SOH + UO_2^{2+} = SOUO_2^{+} + H^{+}$
2	$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^{+}$
3	$SOH + UO_2^{2+} + H_2CO_3 = SOUO_2HCO_3 + 2H^{+}$
4	$SOH + UO_2^{2+} + H_2CO_3 = SOUO_2CO_3^{-} + 3H^{+}$
5	$SOH + UO_2^{2+} + H_2CO_3 + H_2O = SOUO_2OHCO_3^{2-} + 4H^{+}$
6	$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(HCO_3)_2^{-} + 3H^{+}$
7	$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(CO_3HCO_3)^{2-} + 4H^{+}$
8	$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(CO_3)_2^{3-} + 5H^{+}$
9	$SOH + UO_2^{2+} + 2H_2CO_3 + H_2O = SOUO_2OH(CO_3)_2^{4-} + 6H^{+}$