Tank Farm Geochemistry of $^{137}Cs^{+}$

Support by EMSP FY97 – FY00

Focus

- Sorbing phases in pristine/contaminated sediments
- Macroscopic models of the sorption process
- Fixation mechanisms and extent
- Effects of $[OH^{-}]$, $[Al(OH)_4^{-}]$, temperature

Contributors

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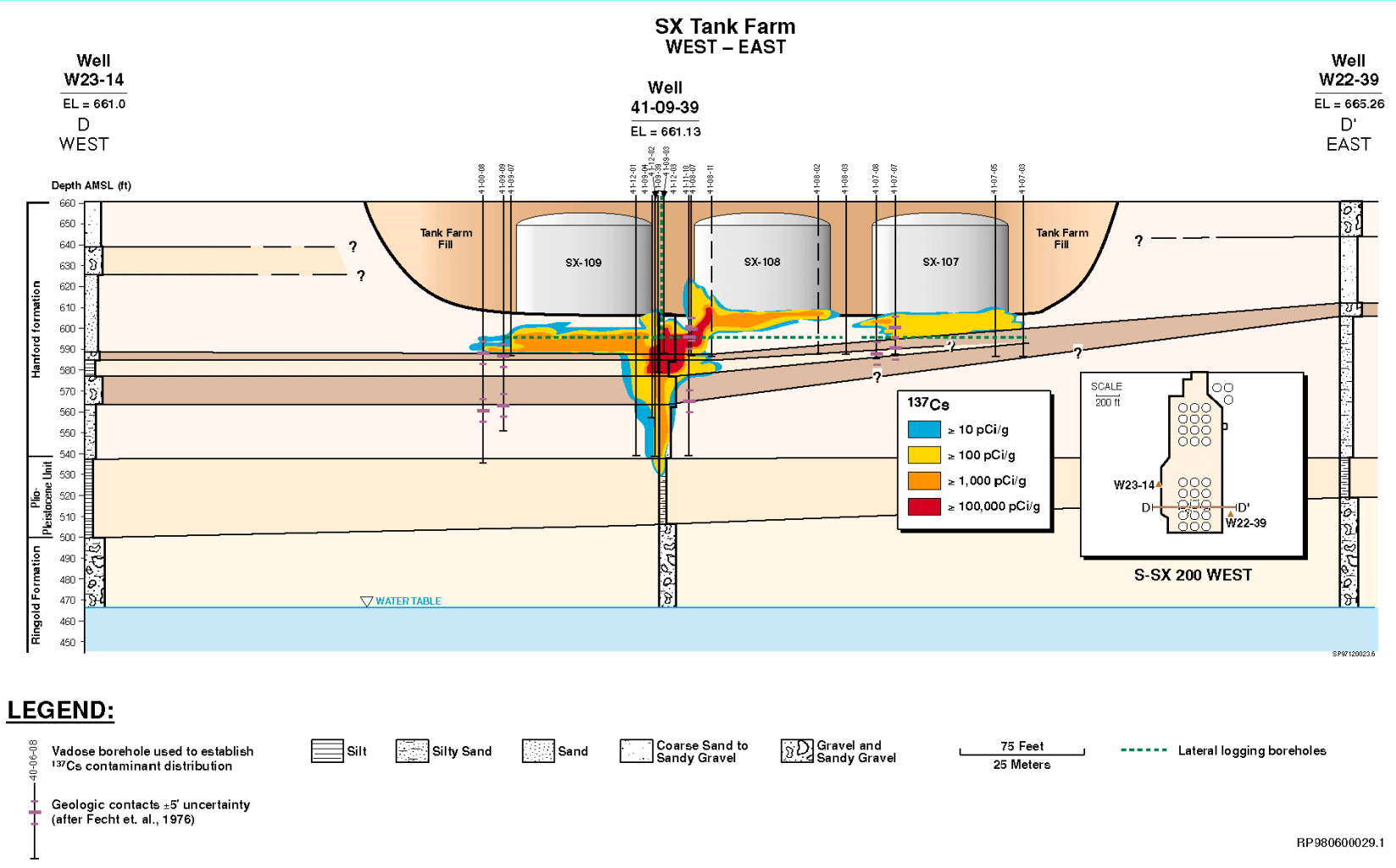
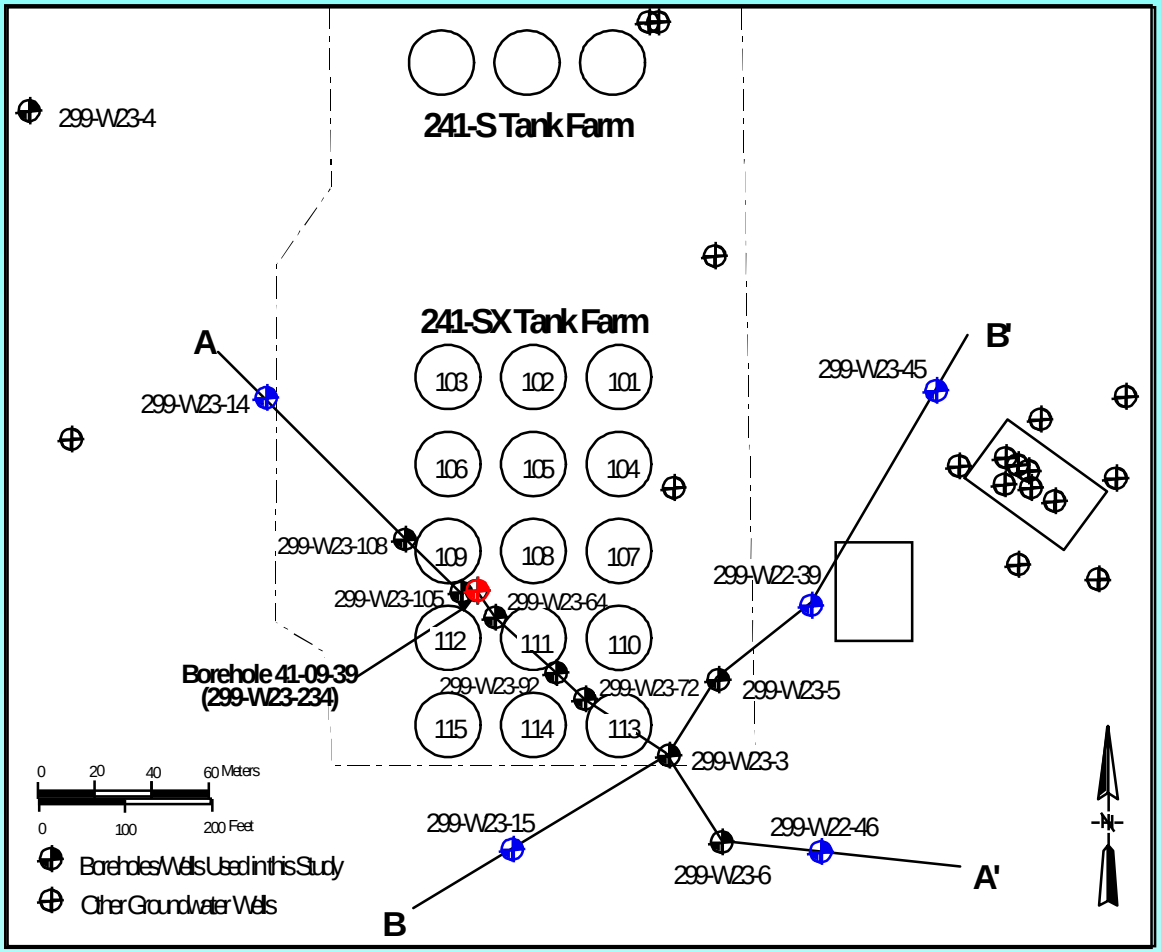
Relationship Between Depth Distribution of Cesium-137 and SX Tank Farm Stratigraphy



Boreholes Used for Composite Samples

Sediment samples from beneath the tank farms are difficult to obtain.

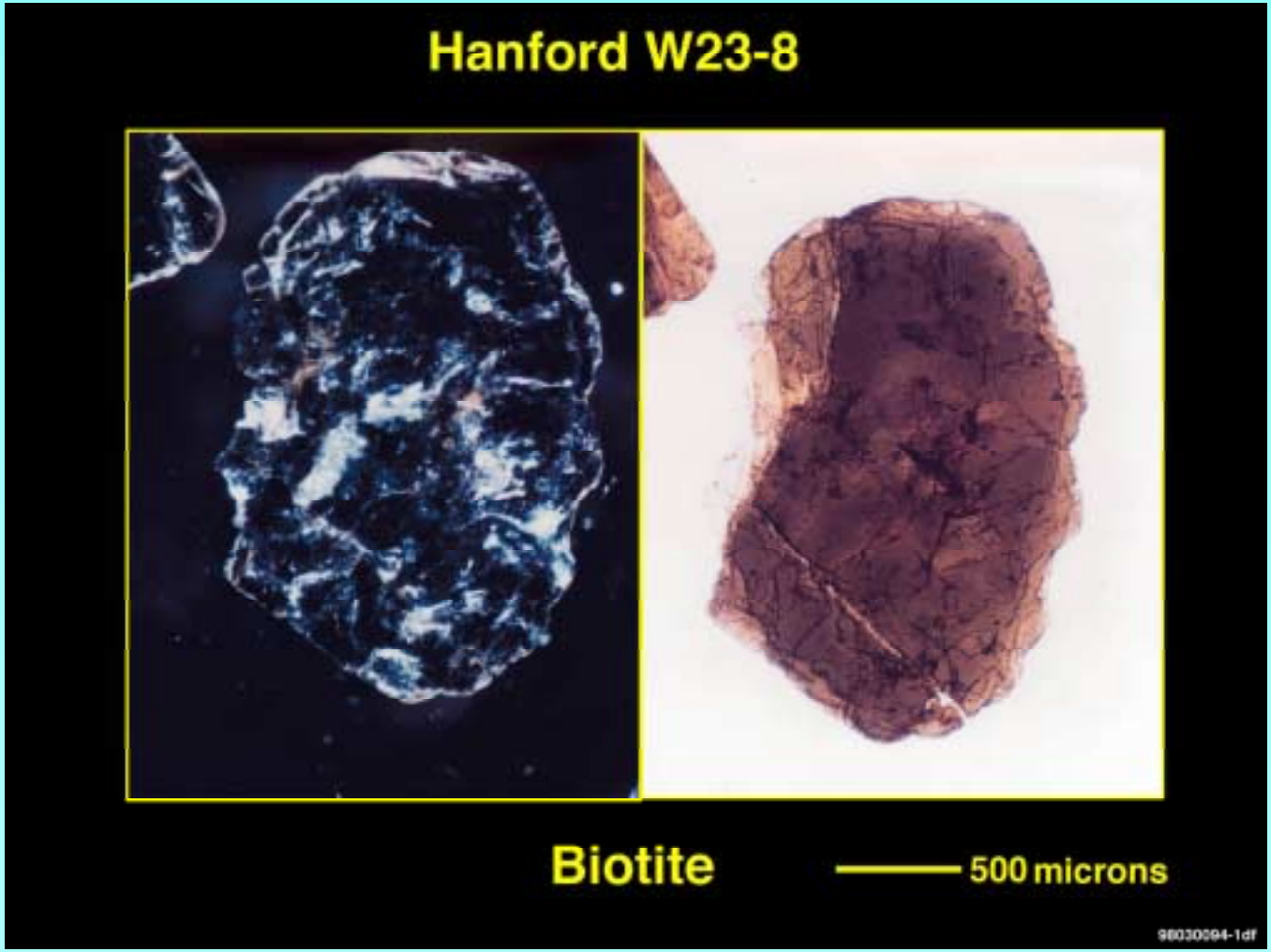
RCRA monitoring wells have been placed around the tank farms and these provide limited volumes of uncontaminated sediments.



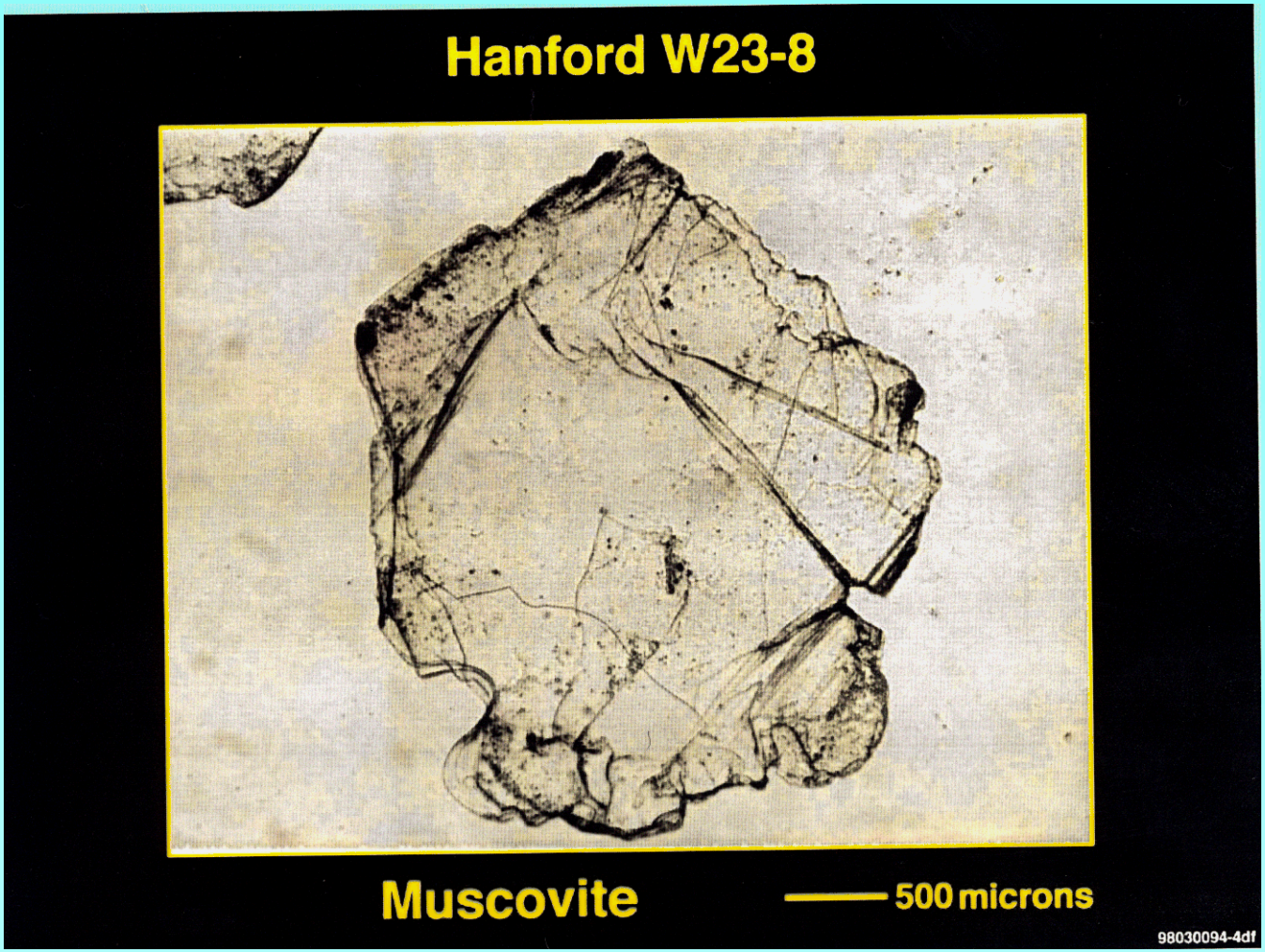
Core Inventory

- A 25 kg reference vadose zone sediment representative of the 17m below the SX farm was created by compositing over 100 core subsamples from the appropriate depth intervals of six wells.
- The reference vadose zone material is called the “Above B” composite.

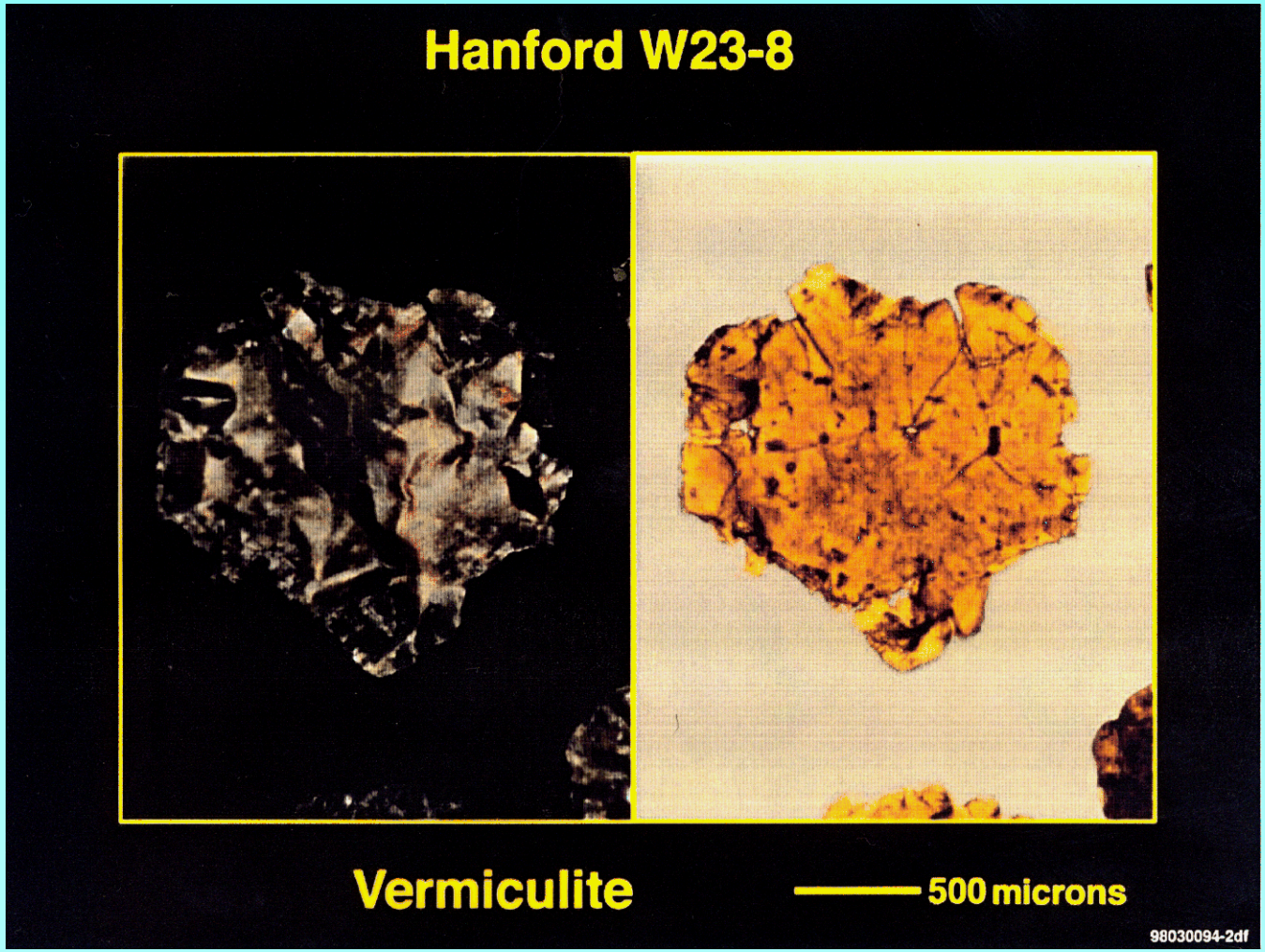
Biotite from ‘Above-B’ Sediment



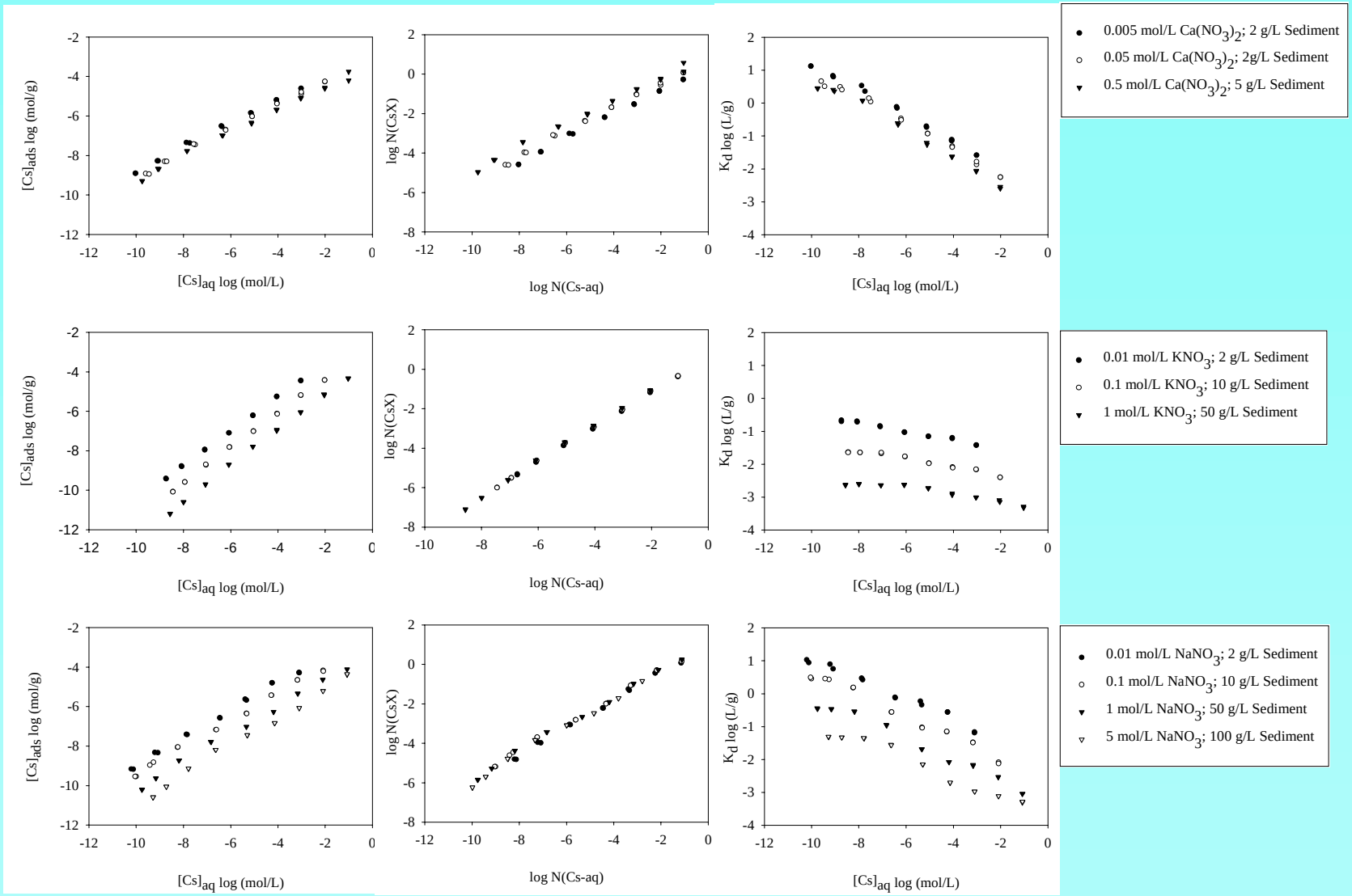
Muscovite from ‘Above-B’ Sediment



Vermiculitized Biotite from ‘Above-B’ Sediment



Adsorption of ^{137}Cs on Hanford Sediment



Conditional Equilibrium or Exchange Coefficients

Global

$$\mu Cs^{+}_{(aq)} + AX_u = uCsX + vA^{ut+}_{(aq)}$$

$$K_c = [A^{ut+}]^v[N_{CsX}]^u/[Cs^+]^u[N_{AX_u}]^v$$

$$N_{CsX} = [CsX]/([CsX] + [AX_u]) \text{ and } N_{AX_u} = [AX]_u/([CsX] + [AX_u])$$

Multisite

$$K^{I}_{c}(Cs^{+}\text{-}A^{+}) = \frac{N^{I}_{Cs}\,[A^{+}]}{N^{I}_{A}\,[Cs^{+}]}$$

$$K^{II}_{c}(Cs^{+}\text{-}A^{+}) = \frac{N^{II}_{Cs}\,[A^{+}]}{N^{II}_{A}\,[Cs^{+}]}$$

Multiple Site Modeling Parameters for Cs^+ Sorption by Illite and the Hanford Sediment

Citation	Site Type	Site Concentration T [1]	Site Concentration Q [2]	Selectivity Coefficient [3] (log K_c)
Brouwer et al., (1983)		CEC_{Na}=1.53 x 10^{-4} eq/g; CEC_{Na}=1.53 x 10^{-4} eq/g		
	FES (type 1)	1.0 x 10^{-6} eq/g (Na)	6.53 x 10^{-3}	Na-Cs = 5.64
		5.0 x 10^{-7} eq/g (K)	2.53 x 10^{-3}	K-Cs = 4.08
	FES (type 2)	5.0 x 10^{-6} eq/g (Na)	3.26 x 10^{-2}	Na-Cs = 2.99
		5.0 x 10^{-6} eq/g (K)	2.53 x 10^{-2}	K-Cs = 1.38
	Planar		0.999	Na-Cs = 1.56
			0.999	K-Cs = 0.65
Poinssot et al., (1999)		CEC_{Na}=1.27 x 10^{-4} eq/g		
	FES	5.5 x 10^{-7} eq/g	4.33 x 10^{-3}	Na-Cs = 6.95±0.2
				K-Cs [5] = 4.70
				Na-K = 2.25±0.4
	Planar	3.5 x 10^{-5} eq/g	2.75 x 10^{-1} [4]	Na-Cs = 3.60±0.2
This study (from Fig. 5)		CEC_{Na}=4.26 x 10^{-5} eq/g; CEC_K=8.25 x 10^{-5} eq/g		
	FES	3.45 x 10^{-8} eq/g (Na)	8.1 x 10^{-4}	Na-Cs = 6.76±0.6
		2.72 x 10^{-8} eq/g (K)	3.3 x 10^{-4}	K-Cs = 4.73±.10
				Na-K [6] = 2.03
	Planar	4.26 x 10^{-5} eq/g (Na)	0.999	Na-Cs = 2.20±.1
		8.25 x 10^{-5} eq/g (K)	0.999	K-Cs = 0.96±.057
				Na-K [6] = 1.24

1 total concentration

2 Q = site concentration/CEC_E, where E is the electrolyte cation

3 $K_c = \frac{N_{CsX}\,[E]^+}{N_{EX}\,[Cs^+]}$, where N = mole fraction and E is electrolyte cation

4 note planar sites << CEC

5 by difference

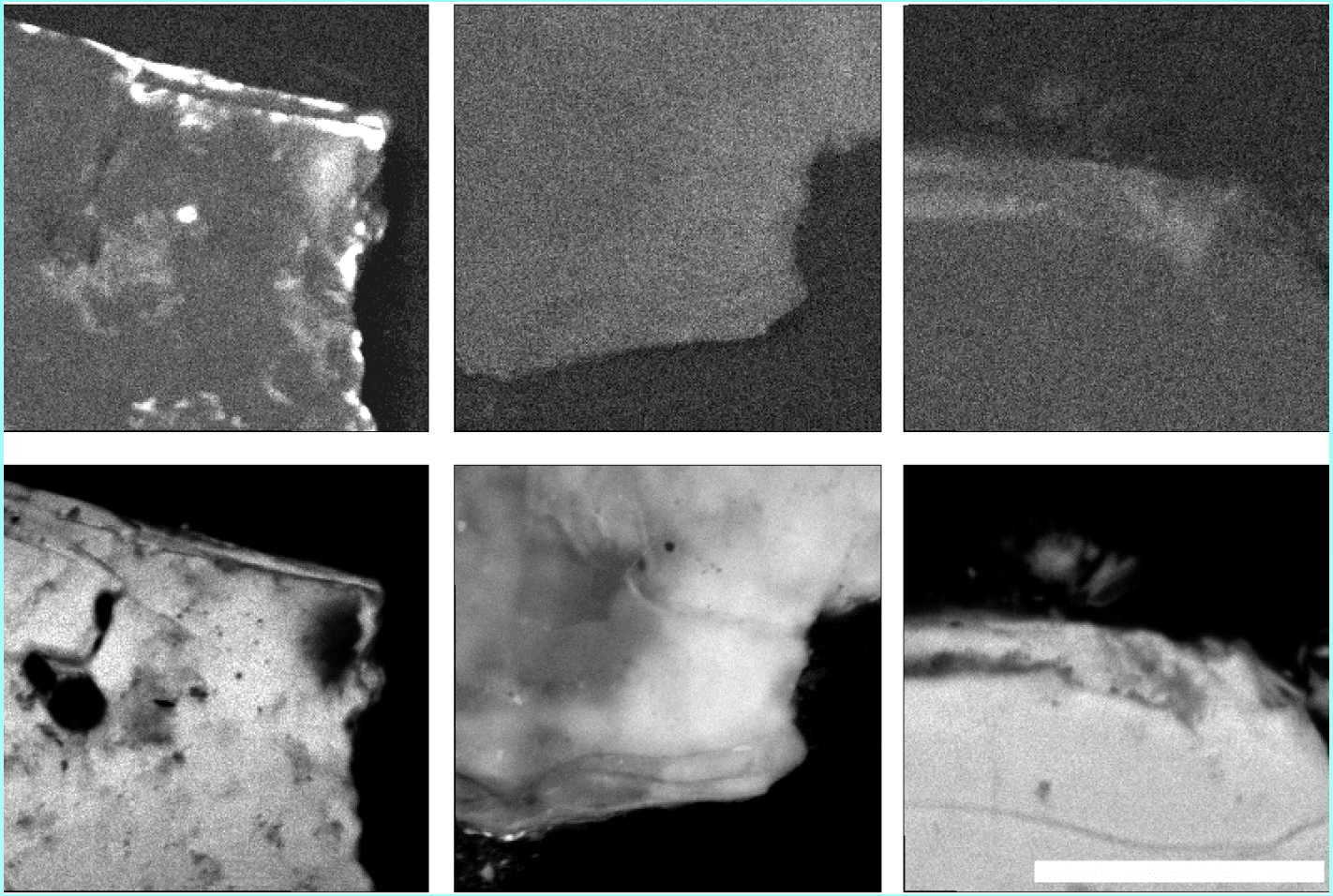
6 by difference

Plan-View Electron Microprobe Analyses of Cs^+-Contacted Micas

a. Biotite b. Vermiculitized Biotite c. Muscovite

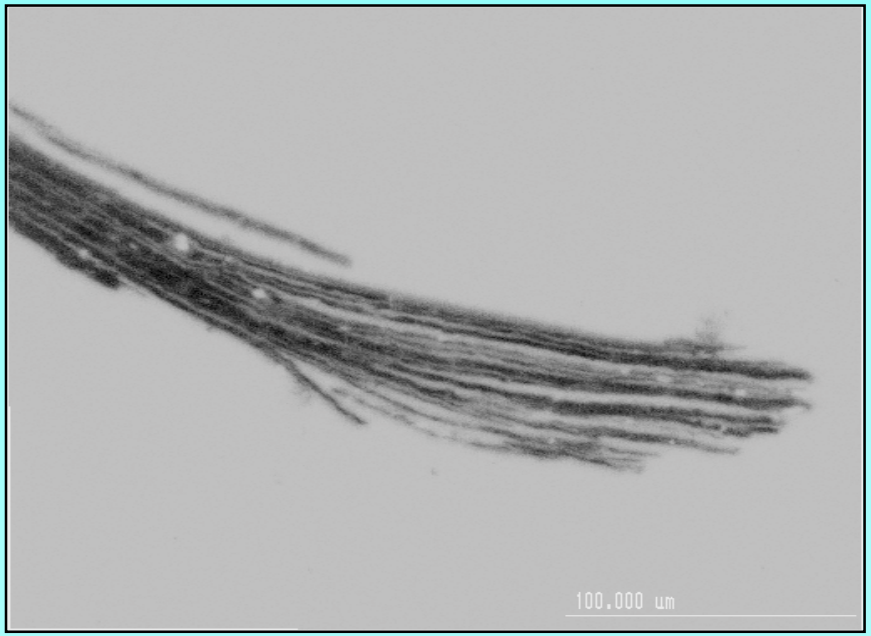
Cs^+ →

K^+ →

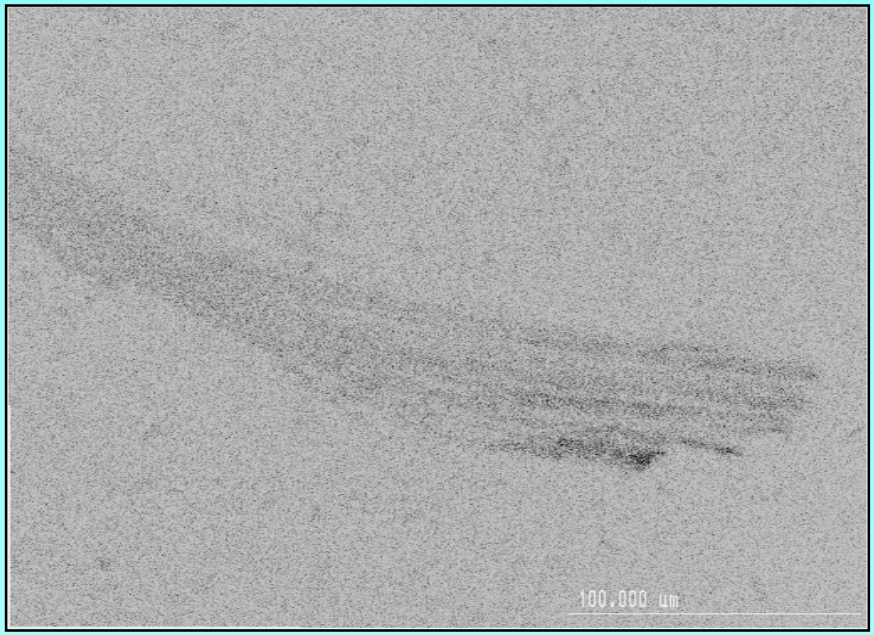


Cross Sectional EMP Analyses of Cs^+-Contacted Micas

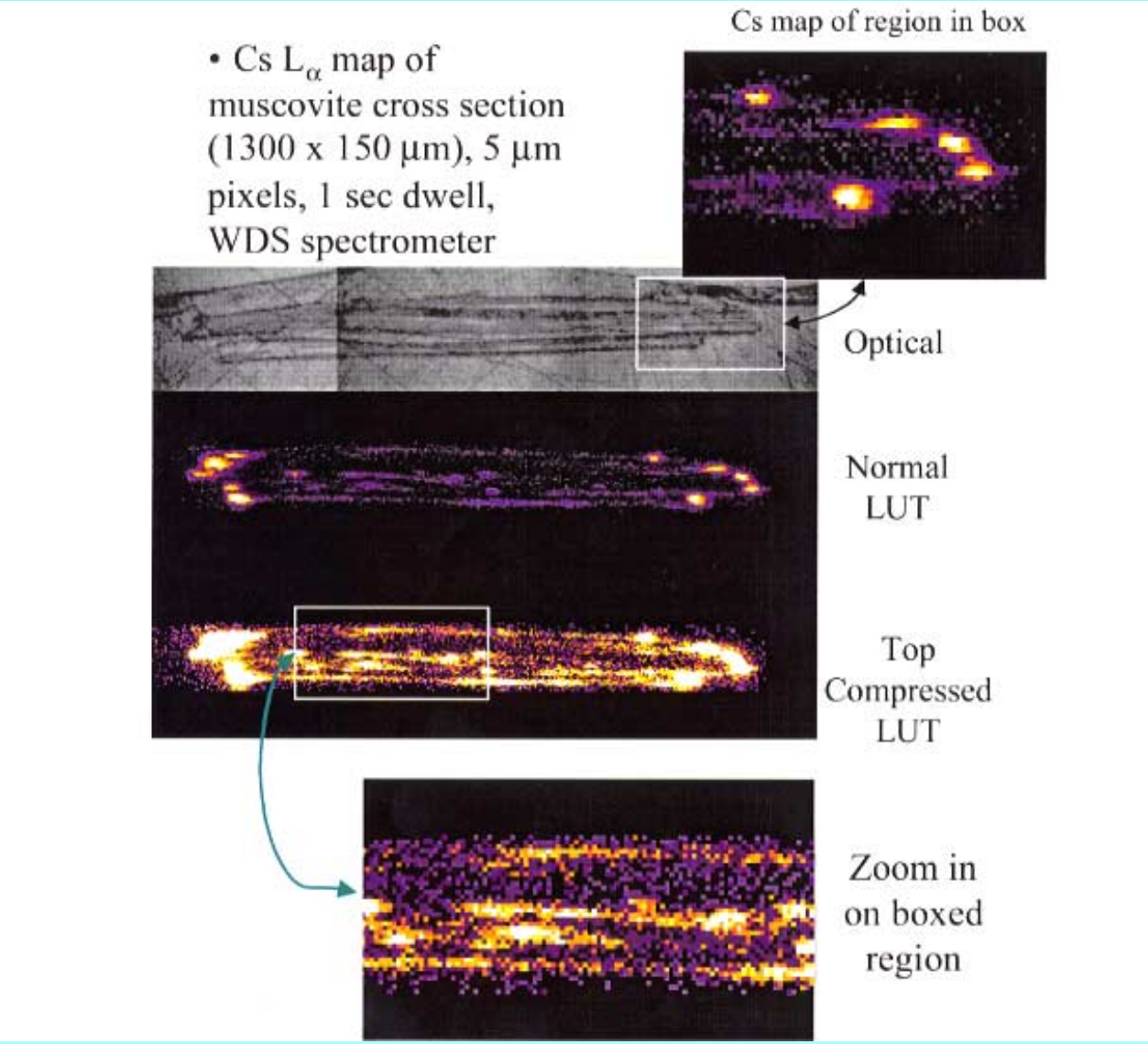
a. K^+



b. Cs^+

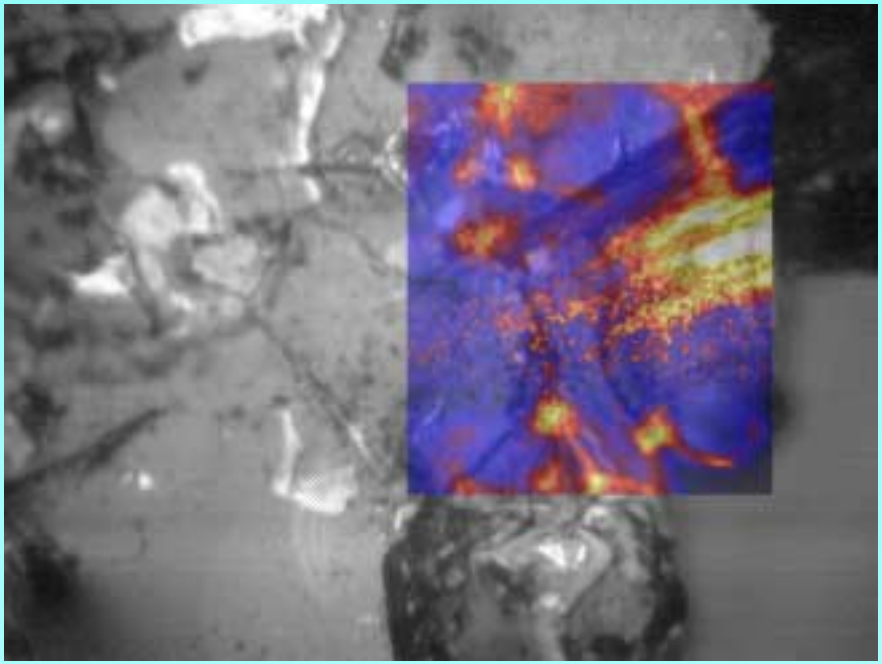


Cesium Incorporation into Phyllosilicates

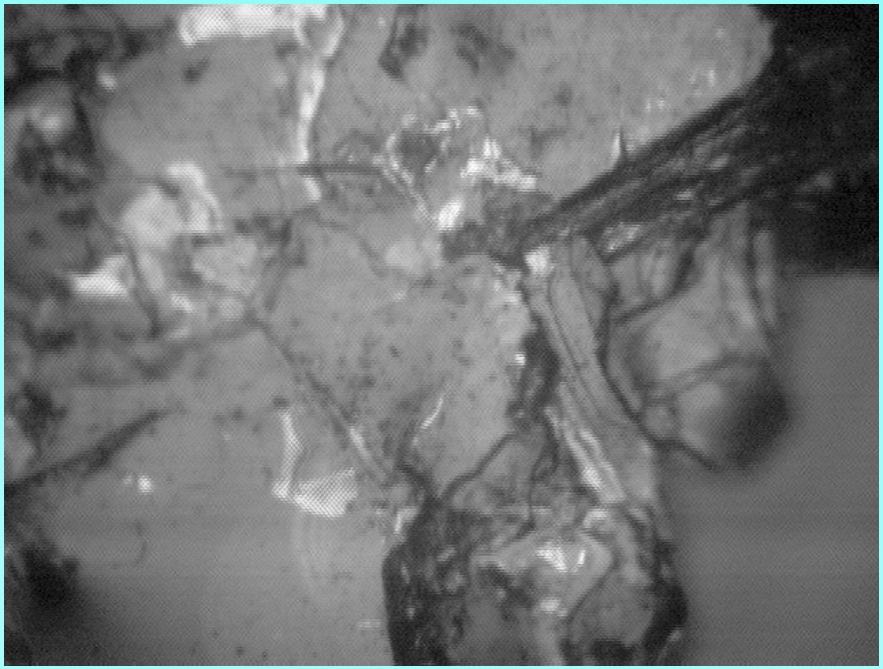


Optical/X-ray Images of Cs Distribution in Micas Exposed to Cs^+

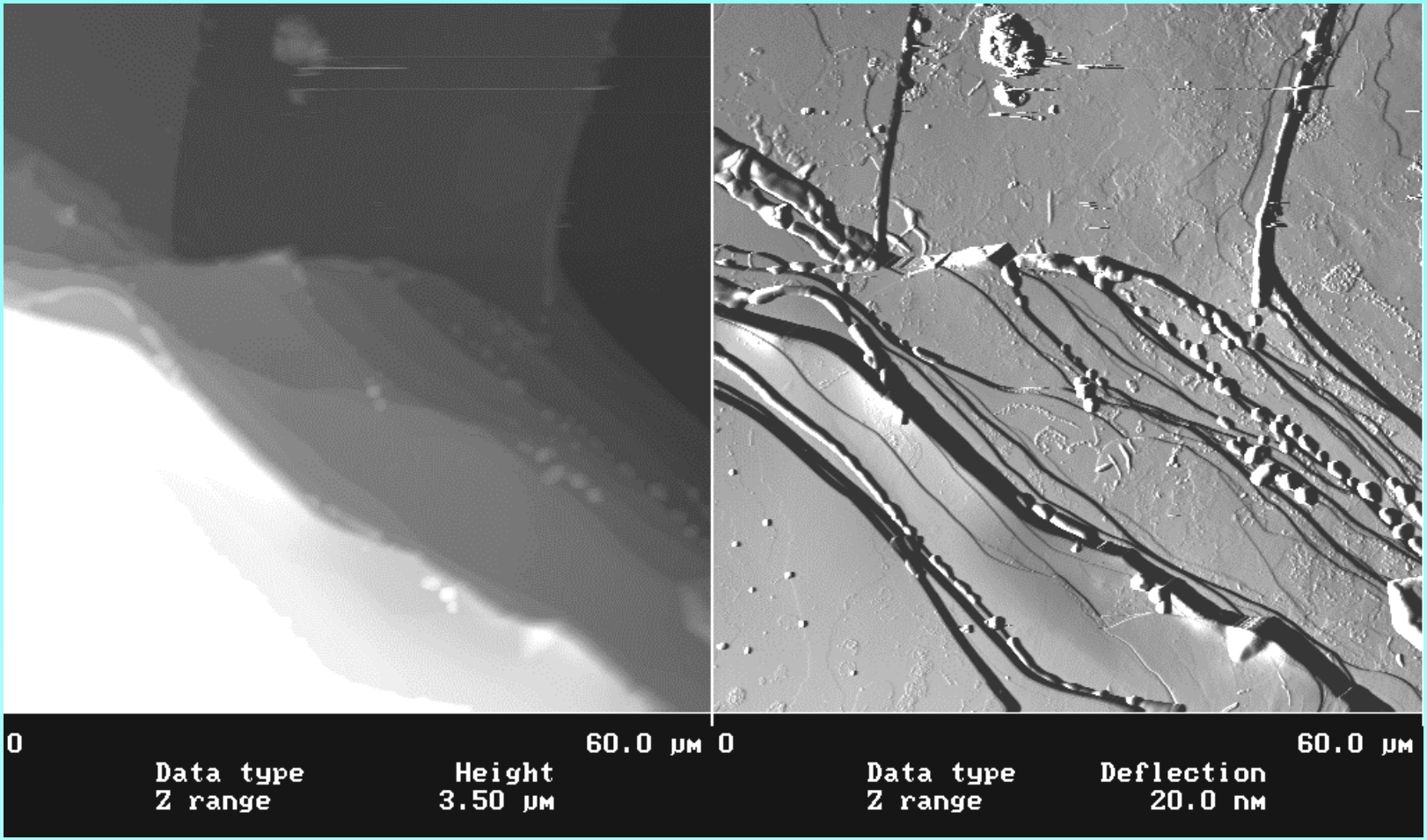
a.



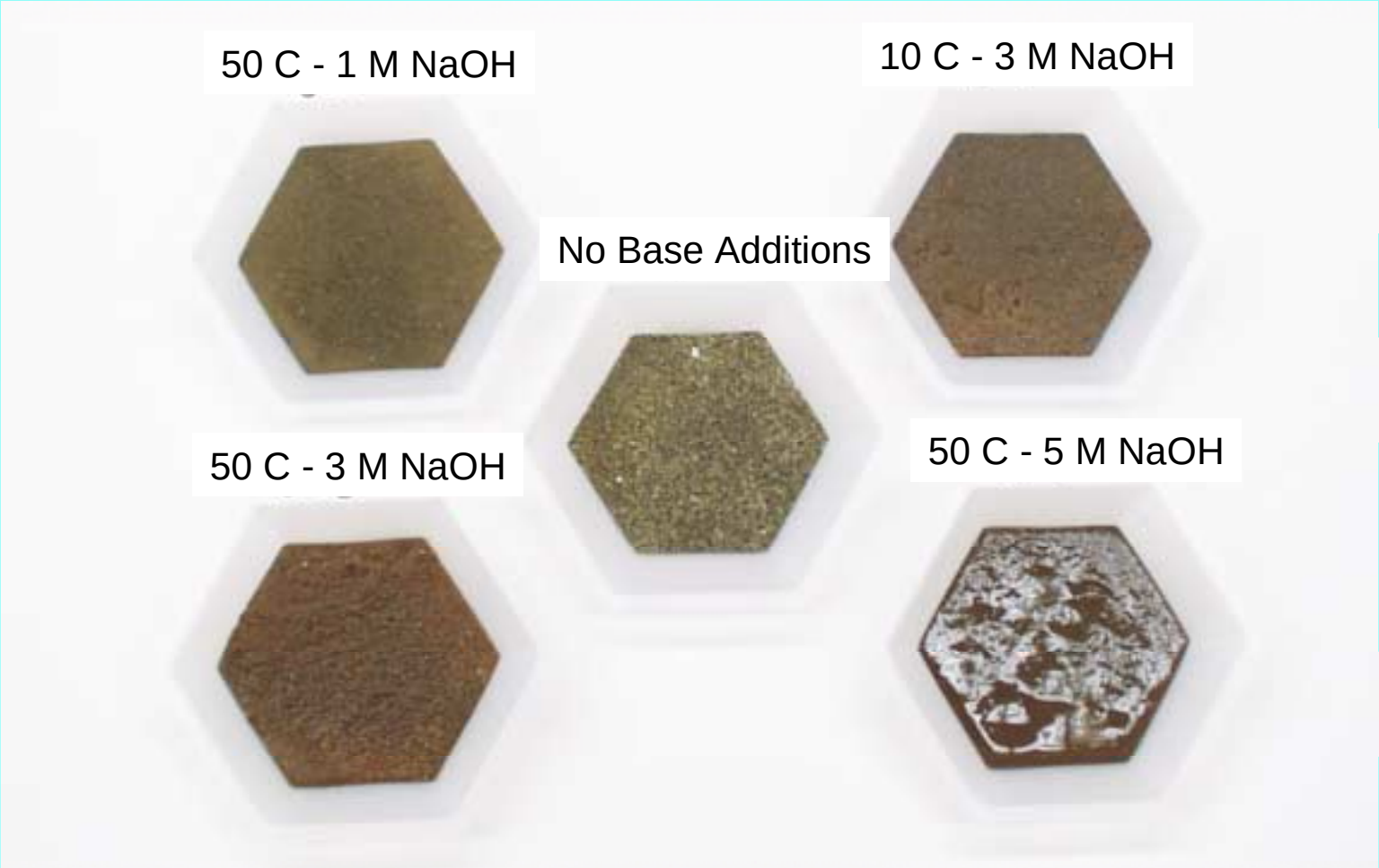
b.



Atomic Force Microscopy of Hanford Mica



Effect of Base Additions and Temperature on the Ringold 'Above B' Sediment

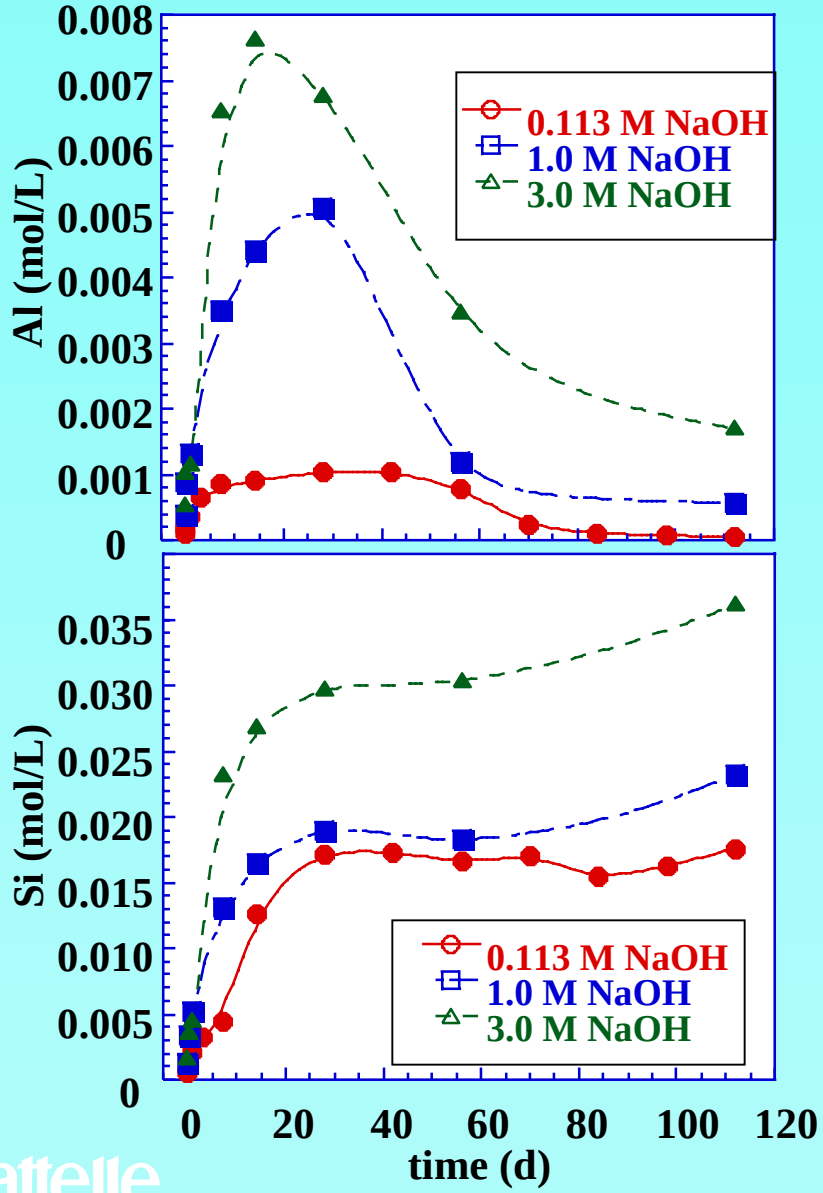


Hanford Sediment Cs Exchange in the Presence of High [OH] and Nitrate Concentrations

Studies Consisted of Batch-Type Experiments

- 1 M $NaNO_3$ at NaOH 0.1M, 1M and 3M NaOH
- Aqueous solution monitored with time
- Cs exchange determined after selected reaction times
- Cs sorption kinetics followed as a function of [OH]

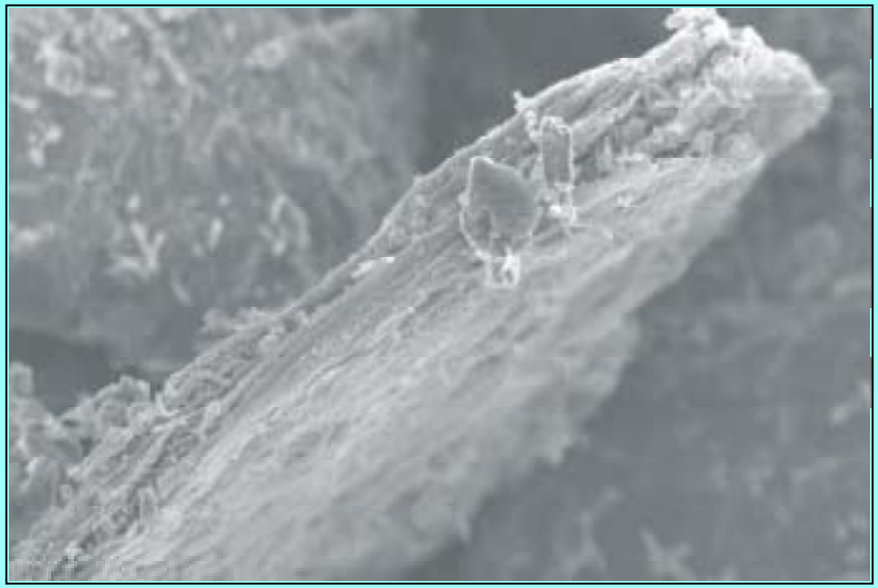
Impact of [OH] on Aqueous Phase Al and Si With Time



- [Al] dependent on time and [OH]
- Appears to reach a supersaturated or nucleation condition
- Prior to Al precipitation, aq. [Si] and [Al] ratio remains constant

Impact of [OH] on Mineralogy

a.



b.

At 0.1M NaOH, XRD analysis shows only limited changes

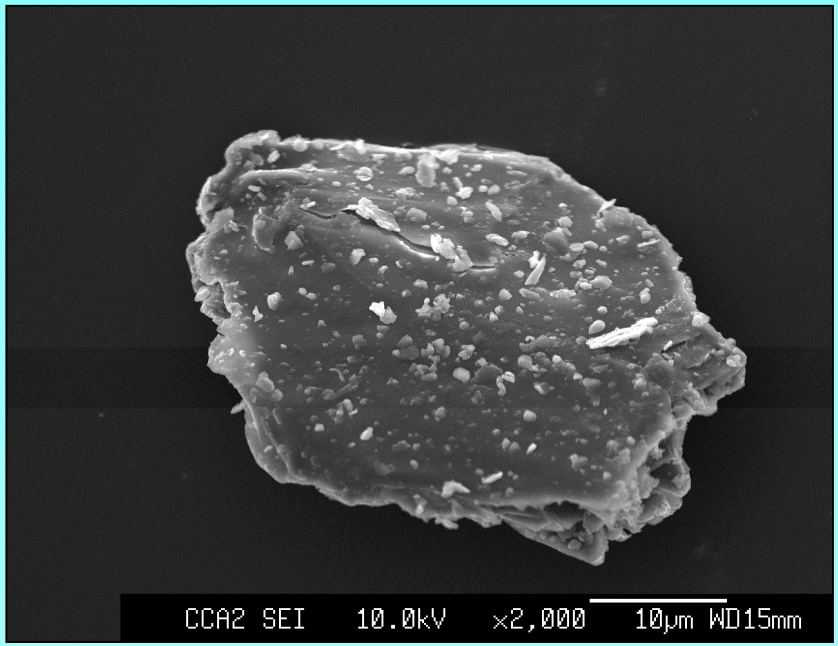
- Possible dissolution of montmorillonite, kaolinite, and micas
- Presence of zeolite (tetranatrolite?) at longer time periods
- CEC increased from 4.26×10^{-5} eq/g to 7.42×10^{-5} eq/g

At higher [OH], mineralogic impacts increased

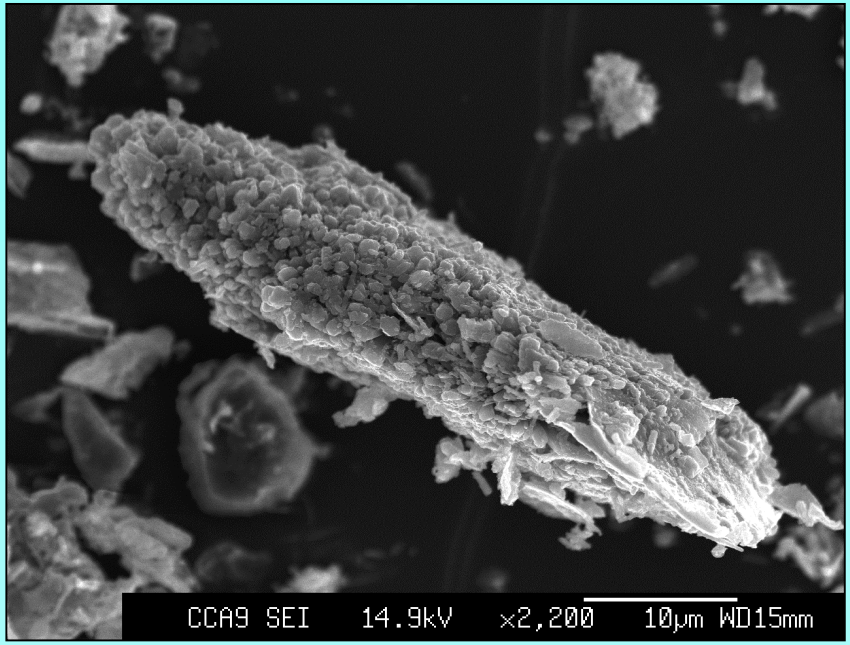
- Complete disappearance of smectites, kaolinite with time (>7 d)
- Increasingly strong zeolite patterns with increasing [OH] and time
- Biotite patterns, with time, suggest dissolution

Mica Particles Before and After Contact with OH^-

a.) before

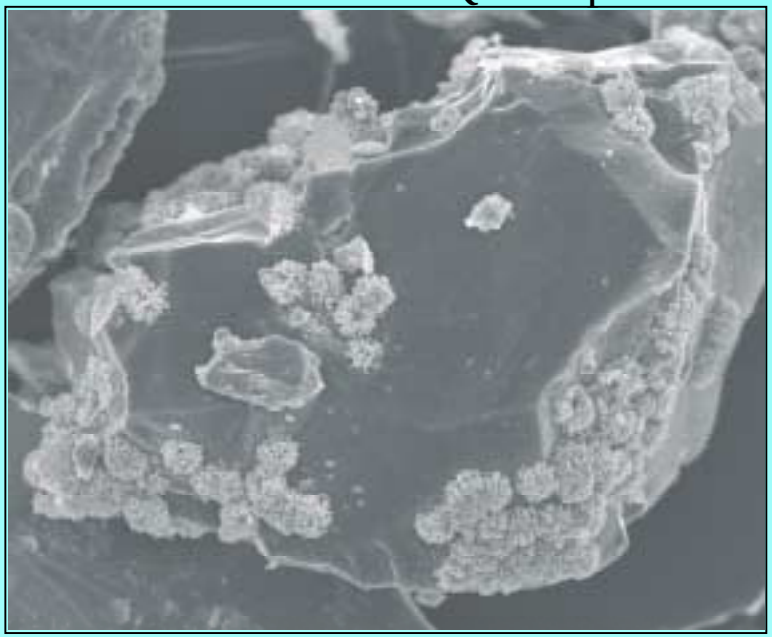


b.) after

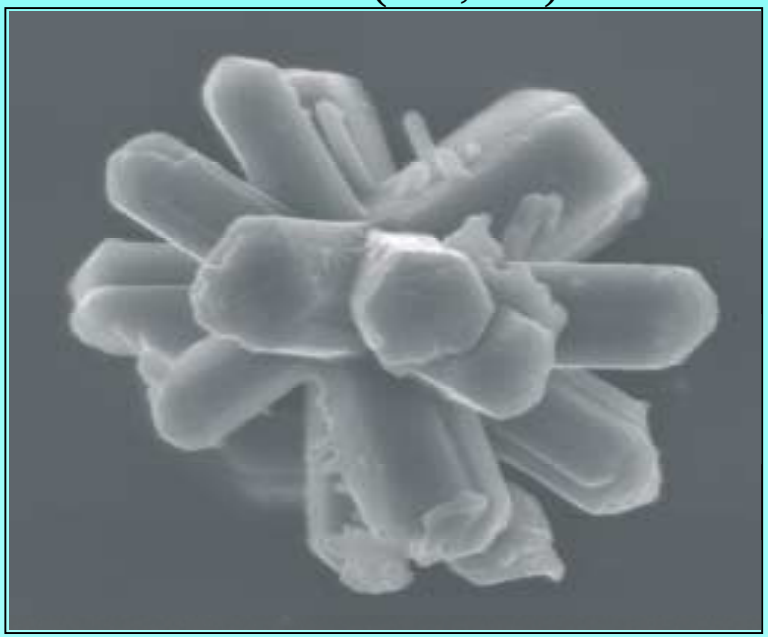


Impact of [OH] on Mineralogy

a. Zeolite Clusters on Quartz particle



b. Zeolite Cluster (x23,000)



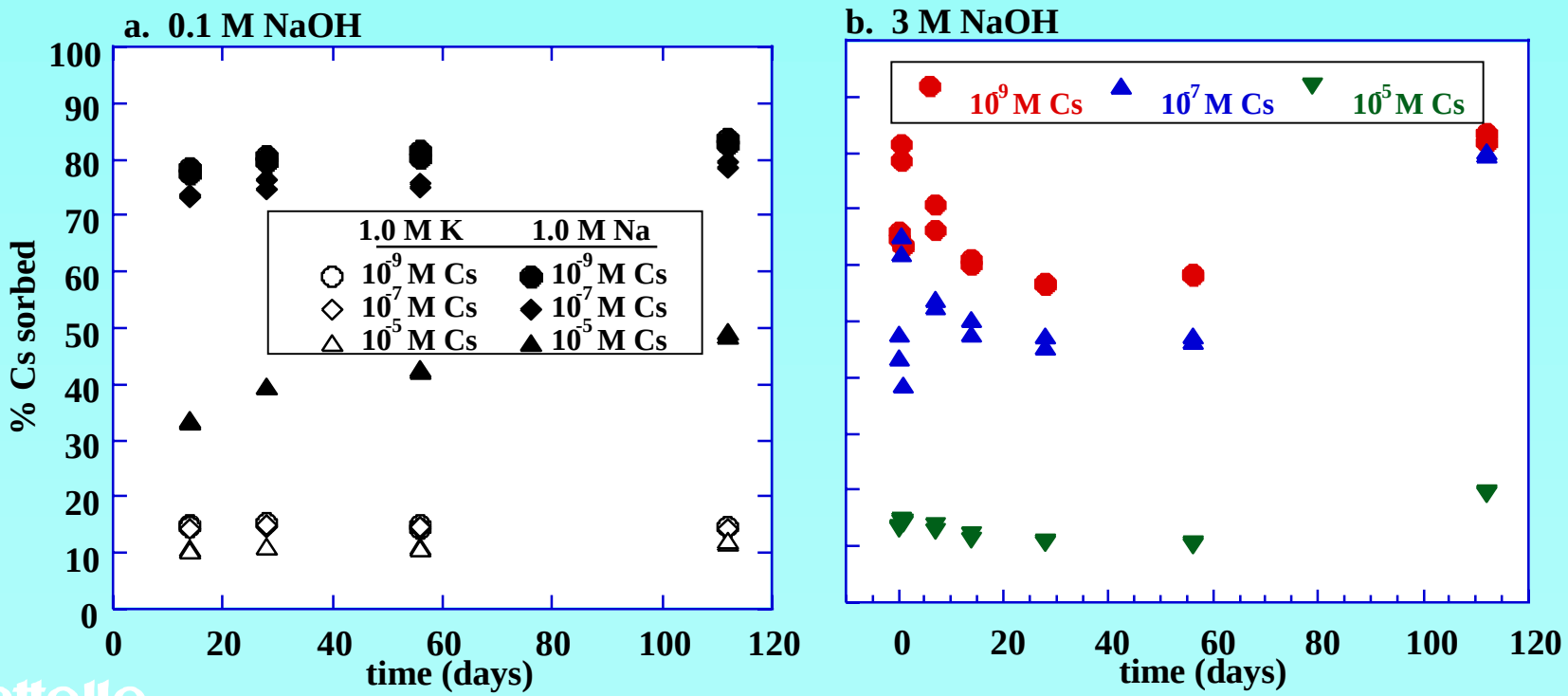
Zeolite production dependent on time and [OH]

- Except at 0.1M NaOH, unnamed zeolite is produced
- Si/Al ratio of zeolites are low (1:1 or 1.5:1)
- Single crystals are observed at short time periods and lower [OH]
- At higher [OH] zeolites form Clusters

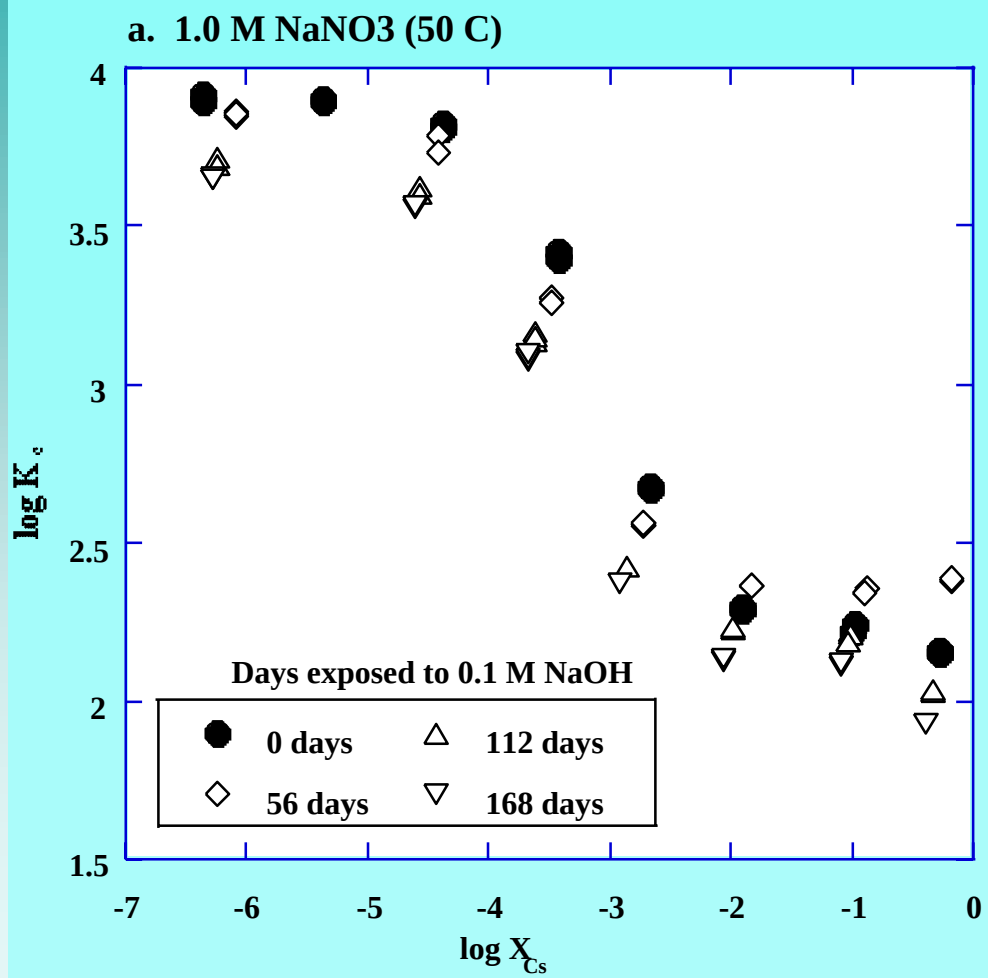
Impact of [OH] on Cs Sorption Kinetics

Cs sorption is dependent on [OH] and time

- 0.1 M – uptake initially rapid followed by slow sorption
  - behavior appears to follow increase in CEC
  - K+ competes with Cs for exchange sites
- 1 and 3 M [OH] – Cs sorption is affected by clay dissolution and micas interlayers opening up and creating new exchange sites
- No evidence of zeolite production affecting Cs sorption

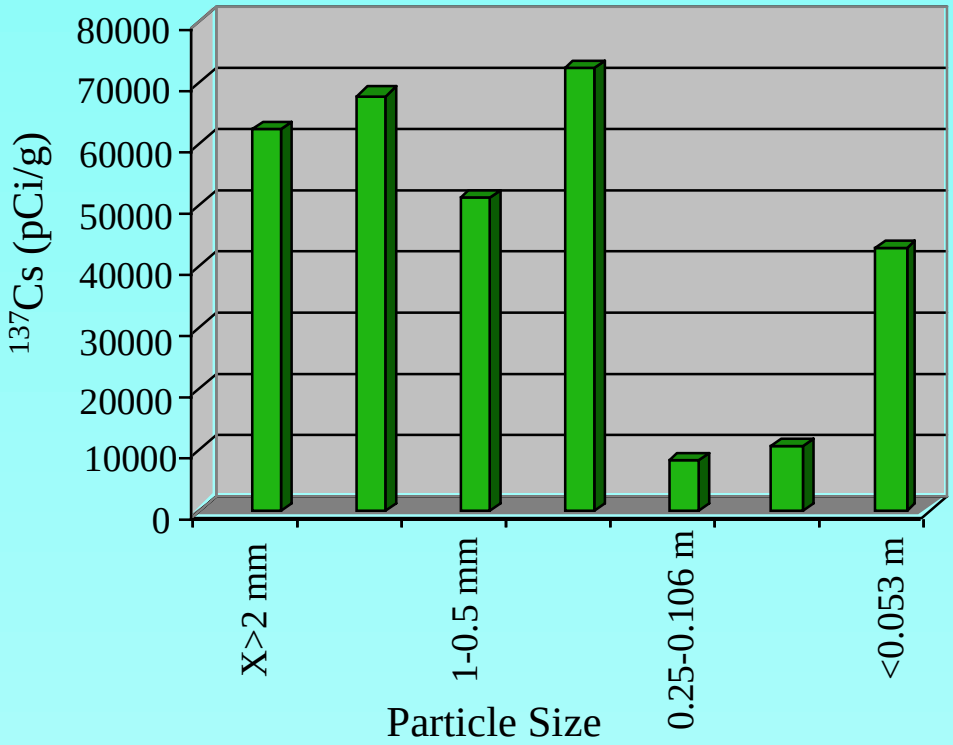


Impact of [OH] on Cs Exchange



- With time, [OH] tends to depress the Cs K_c over the entire exchange isotherm
- Greater impact seen at lower X_{Cs} levels probably related to disruption of FES
- K_c reflects the change in CEC with time, 4.26×10^{-5} eq/g to 7.42×10^{-5} eq/g

^{137}Cs vs Particle Size Composite 2C/2D



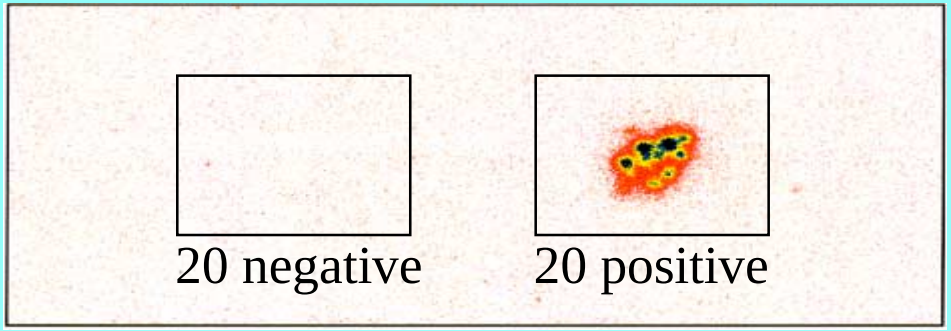
	mass%	pCi/g - ^{137}Cs	pCi/- %
x > 2mm	2.15	62200	3.92
very coarse sand	2.58	68000	5.14
coarse sand	3.48	51300	5.23
medium sand	1.92	72200	4.06
fine sand	12.8	8010	3.00
very fine sand	28.0	10700	8.77
silt/clay	47.9	42800	60.0
bulk sample		34150	

- Particle size fractionation was performed by wet sieving and the samples were counted
- The highest specific activity of ^{137}Cs was found in the sand fractions that contain mm sized mica flakes
- Most of the adsorbed ^{137}Cs was found in the silt/clay because of its high mass % and surface area

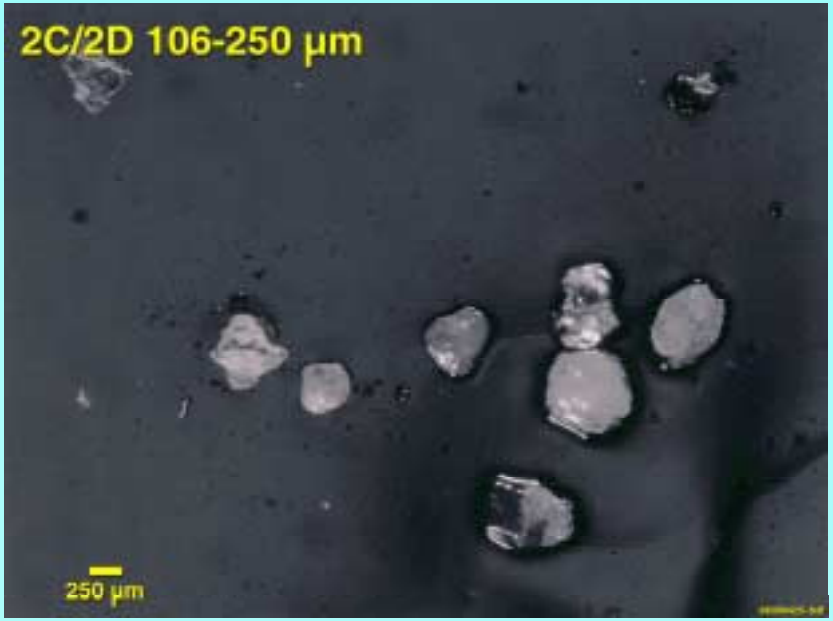
“Hot” and “Cold” Particles from SX-41-09-39

[SX-109 extension; 53-106 µm; 70,000 pCi/g]

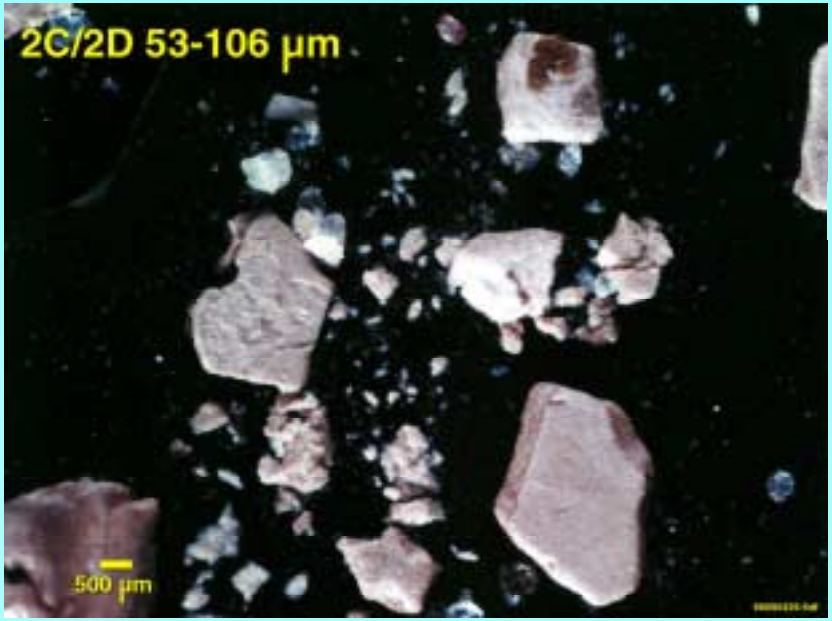
Phosphor Image



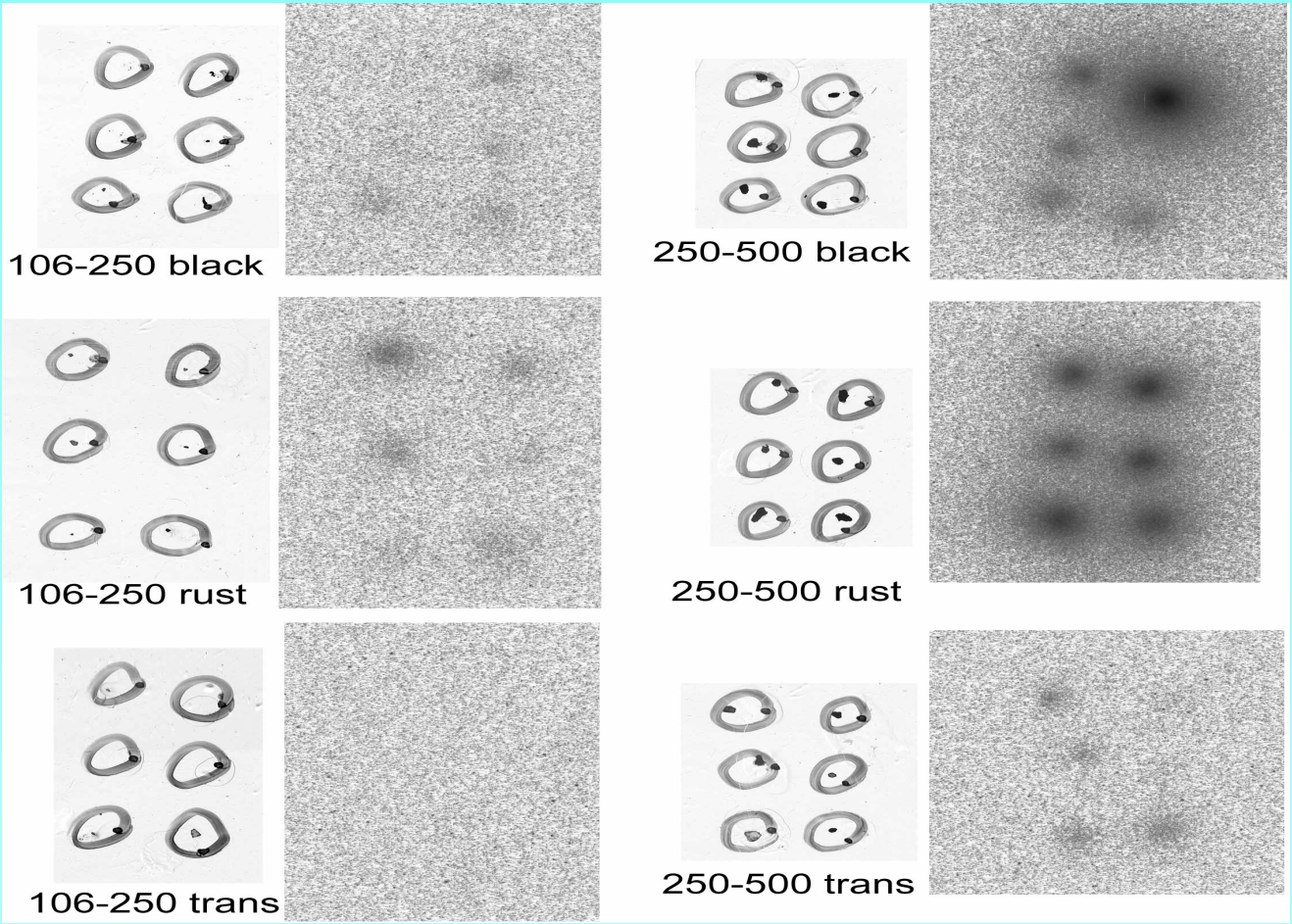
Cold



Hot



Phosphor Images of Hand-Picked Micas from WMA-S-SX Borehole 29-09-39



Findings to Date

- $^{137}Cs^{+}$ is adsorbed by the phyllosilicate fraction
  - Smectite (low affinity)
  - Micas (high affinity)
    - + Biotite > vermiculitized biotite > muscovite

- High affinity sites control Cs^{+} sorption from high salt solutions
  - 3.45×10^{-8} eq/g
  - 10^{8} pCi/g – $^{137}Cs = 8.43 \times 10^{-9}$ mol/g = 24.4% (HAS)

- Key geochemical controls on $^{137}Cs^{+}$ sorption/mobility
  - Electrolyte concentration and identity
    - $K^{+} >> Na^{+} \geq Ca^{2+}$
  - $^{137}Cs^{+}$ concentration
  - Site concentration and [HAS]/[LAS]

- "Fixation" issue unresolved
  - Short term ≠ long term observation

Future Studies

FY01 – FY03

"Fixation Mechanisms and Desorption Rates of Sorbed Cs in High Level Waste Contaminated Subsurface Sediments: Implications to Future Behavior and In-Ground Stability"

- Focus on contaminated sediments from different waste sources and chemistries
  - + SX-108
  - + BX-102
  - + T-106
- Fully characterize mineralogic residence, intra-particle distribution, and sorbent characteristics
  - + phosphor imaging
  - + XAS, TEM, SEM, SIMS
- Investigate desorption kinetics under a range of conditions
  - + electrolyte composition, temperature, extractants/complexants
- Develop a kinetic release model that builds on past studies