

# Role of clay minerals in controlling the fate and transport of radioactive $^{137,134}\text{Cs}$ in soils

30 May 2011

University of Tokyo

Cliff T. Johnston<sup>1</sup> & Stephen F. Agnew<sup>2</sup>

<sup>1</sup>*Purdue University, West Lafayette, IN*

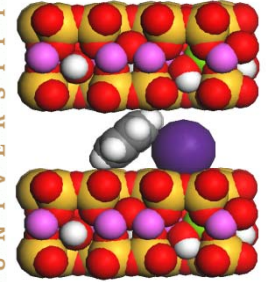
<sup>2</sup>*Columbia Energy & Environmental Services*

**PURDUE**  
UNIVERSITY

 **Columbia Energy**  
AND ENVIRONMENTAL SERVICES

# Overview

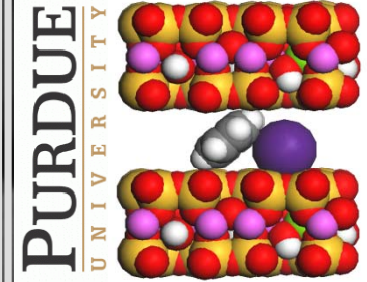
PURDUE  
UNIVERSITY



- Fukushima accident
- Movement of  $^{137}\text{Cs}$  in soils
- Behavior of  $^{137}\text{Cs}$  in soils
- Molecular Interactions of Cs with clay minerals



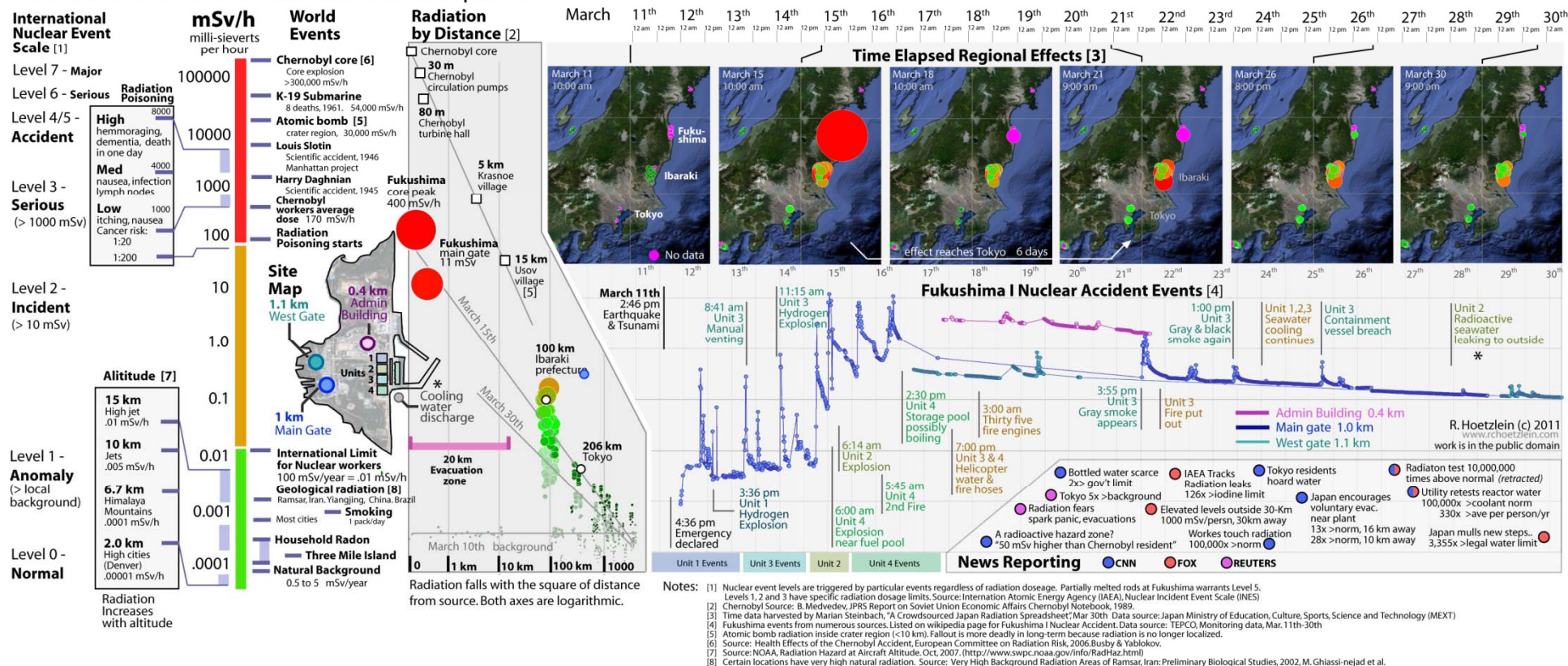
# Fukushima Accident



- Largest recorded earthquake in Japanese history (force of 9.0 Richters).
- Largest Tsunami in Japan's recorded history, 30 ft high, struck that same northeastern shore.
- That cooling failure resulted in the release of a large amount of radiation into the air, ocean, and groundwater.
- Development of new technology needed to remediate contaminated soil in Fukushima prefecture.

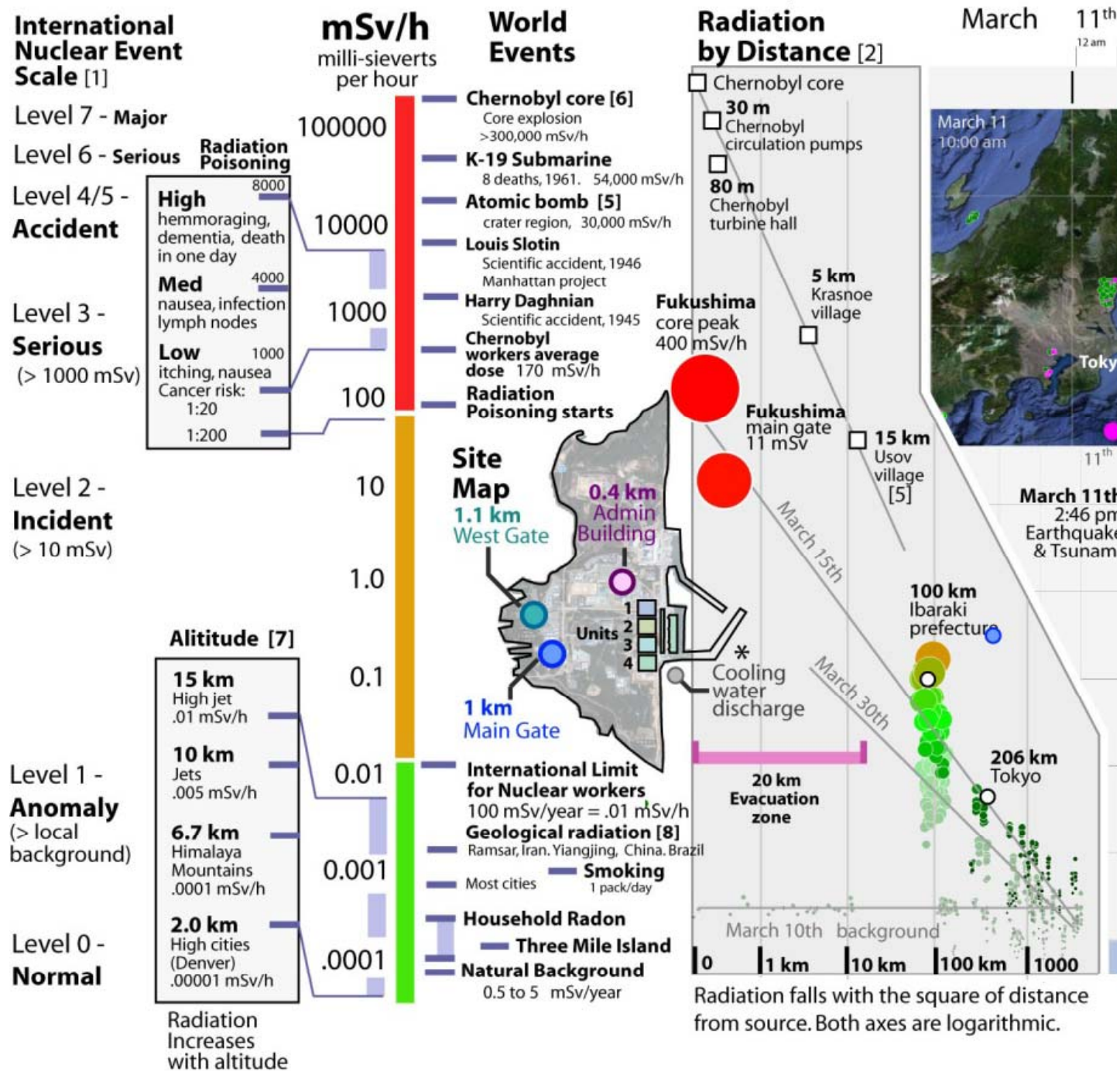


## Fukushima Nuclear Accident - Radiation Comparison



<http://www.rchoetzlein.com/theory/wp-content/uploads/2011/03/fukushima7.jpg>



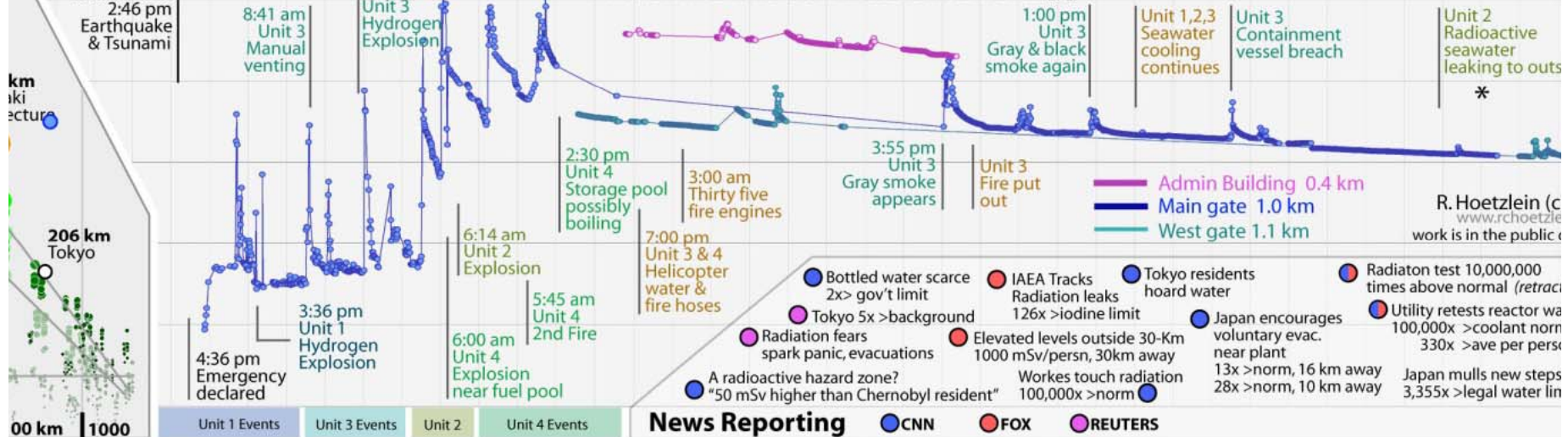


March 11<sup>th</sup> 12<sup>th</sup> 13<sup>th</sup> 14<sup>th</sup> 15<sup>th</sup> 16<sup>th</sup> 17<sup>th</sup> 18<sup>th</sup> 19<sup>th</sup> 20<sup>th</sup> 21<sup>st</sup> 22<sup>nd</sup> 23<sup>rd</sup> 24<sup>th</sup> 25<sup>th</sup> 26<sup>th</sup> 27<sup>th</sup> 28<sup>th</sup> 29<sup>th</sup>

### Time Elapsed Regional Effects [3]



### Fukushima I Nuclear Accident Events [4]



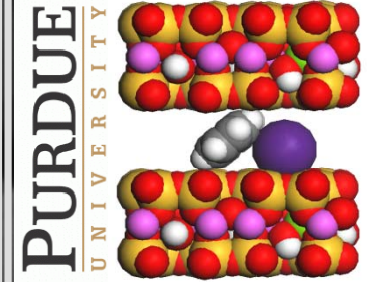


Recent soil assays taken from different directions about 1,000 m from the power station.

[http://www.tepco.co.jp/en/press/corp-com/release/betu11\\_e/images/110525e11.pdf](http://www.tepco.co.jp/en/press/corp-com/release/betu11_e/images/110525e11.pdf)

Sampling spot	Fixed point ①]*1 Playground (west-northwest approx. 500m) *2		Fixed point ②]*1 Forest of wild birds (west approx. 500m) *2		Fixed point ③]*1 Adjacent to industrial waste disposal facility (south-southwest approx. 500m) *2	
Date of sampling	5/ 9	5/12	5/ 9	5/12	5/ 9	5/12
Analyses Organization	JCAC *3	JAEA	JCAC *3	JAEA	JCAC *3	JAEA
Date of analysis	5/11	5/13	5/11	5/13	5/11	5/13
Nuclide-131(approx. 8 days)	9.4E+04	9.4E+04	2.0E+04	9.9E+03	9.1E+04	1.1E+05
(Half-life-132(approx. 2 hours)	ND	ND	ND	ND	ND	ND
Cs-134(approx. 2 years)	5.0E+05	5.0E+05	3.8E+04	1.4E+04	1.1E+05	1.4E+06
Cs-137(approx. 30 years)	5.0E+05	5.2E+05	4.0E+04	1.5E+04	1.1E+05	1.4E+06
Te-125m(approx. 81 days)	1.2E+03	1.6E+03	7.3E+04	3.3E+03	2.7E+03	4.3E+03
Te-132(approx. 3 days)	ND	ND	ND	ND	ND	ND
Ba-140(approx. 13 days)	ND	ND	ND	ND	ND	ND
Nb-95(approx. 35 days)	ND	1.3E+03	ND	ND	ND	1.2E+03
Ru-106(approx. 370 days)	ND	ND	ND	ND	ND	ND
Mo-99(approx. 66 hours)	ND	ND	ND	ND	ND	ND
Tc-99m(approx. 6 hours)	ND	ND	ND	ND	ND	ND
La-140(approx. 2 days)	ND	ND	ND	ND	ND	ND

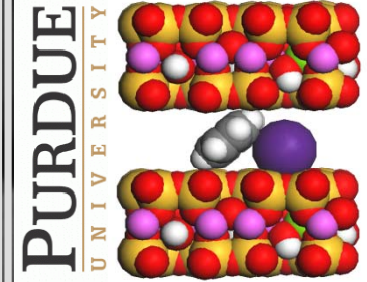
## Recent soil assays



- Cs-137 ranges from 1.4 to 0.014 MBq/kg wet soil (1000 m from the power station)
- For comparison, the Chernobyl typical soil is around 0.3 MBq/m<sup>3</sup> in 2002, which is 180 Bq/kg dry soil at 1700 kg/m<sup>3</sup>.
- [http://www.energy.gov/news/documents/040711\\_\\_AMS\\_Data\\_April\\_7\\_\\_v3.pptx](http://www.energy.gov/news/documents/040711__AMS_Data_April_7__v3.pptx)

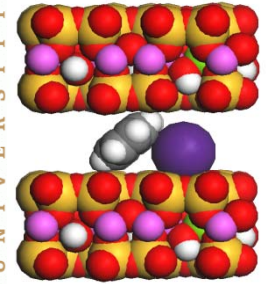


# Radiation Maps



- Result of an aerial survey by DOE NNSA with their special plane.
- Collaboration with Japan's Nuclear and Industrial Safety Agency (NISA)
- Some contamination extends beyond the 30 km limit.

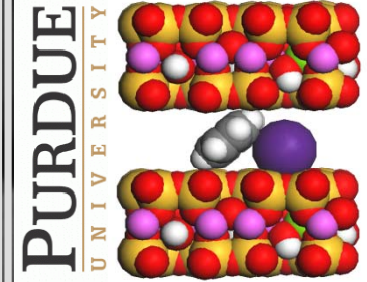




- Aerial Measuring Systems have totaled more than 262 flight hours in support of aerial monitoring operations
- NNSA's Consequence Management Response Teams have collected approximately 100,000 total field measurements taken by DOE, DoD, and Japanese monitoring assets
- 240 total air samples taken at US facilities throughout Japan undergoing lab analysis in the US

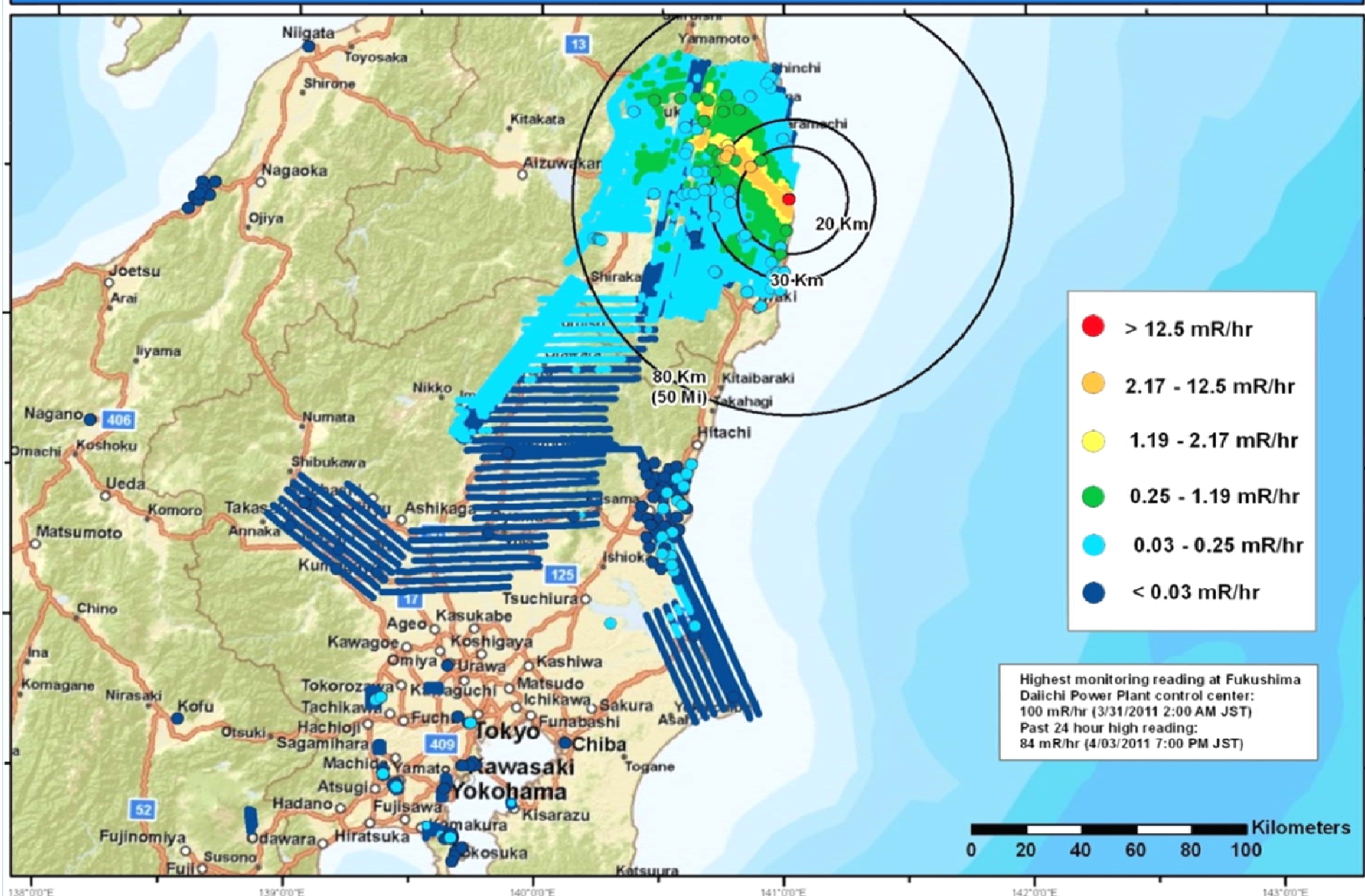


# Guide to Interpretation

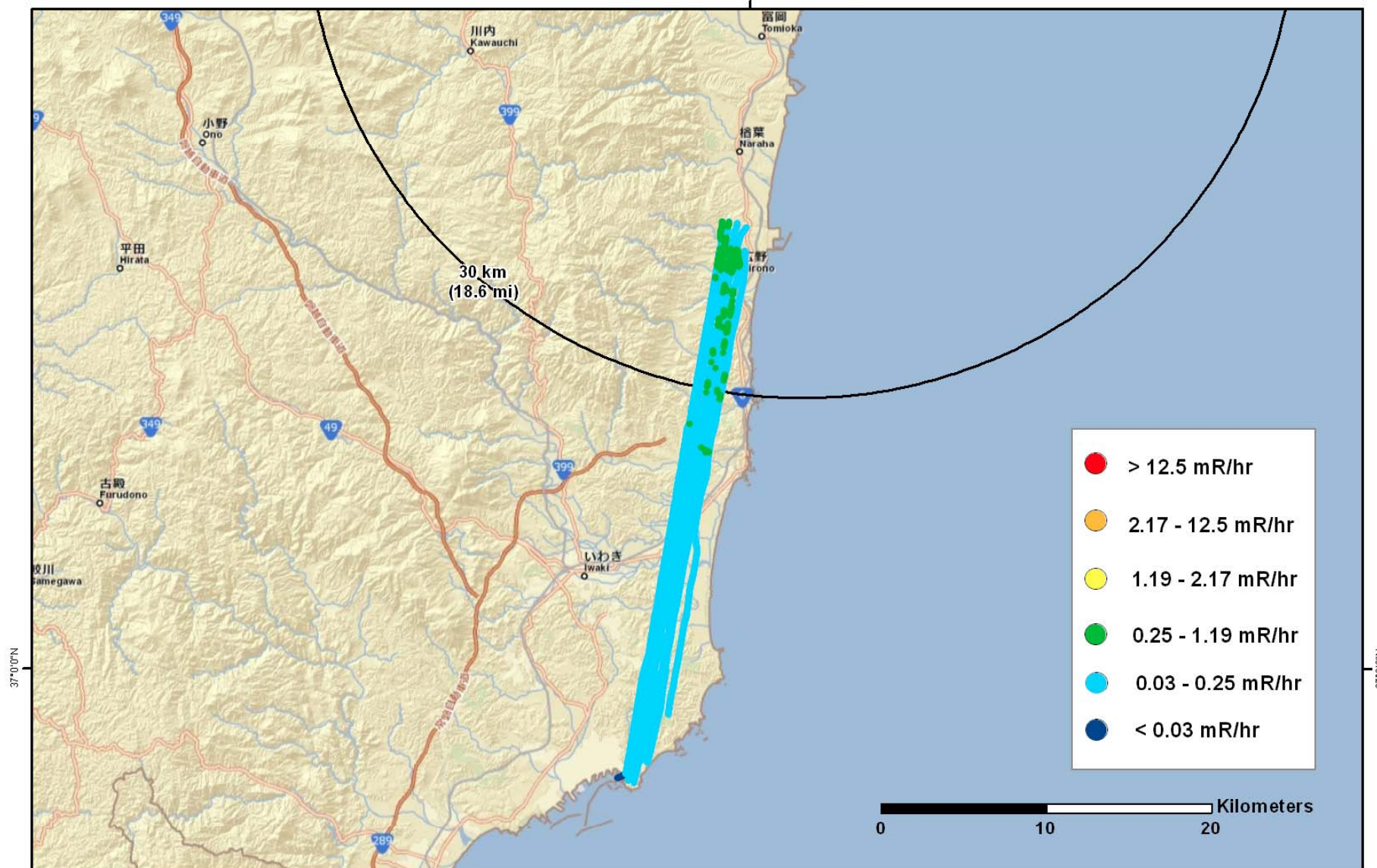


- US radiological assessments are composed of aerial and ground measurements and indicate radiation levels from material that has settled on the ground
- Each measurement corresponds to the radiation a person receives in one hour at that location. AMS data is presented as exposure rate 1 meter from the ground at the time the measurements occurred
- All measurements outside the Fukushima power plant site boundary are below 0.013 REM per hour – a low but not insignificant level









**Map created on 04062011 2300 JST**  
Name: NIT UH-1 Flight 2 Results 06Apr2011

141°0'0"E

NIT  
J

## **Assessment:** Measurements gathered through April 6 continues to show:

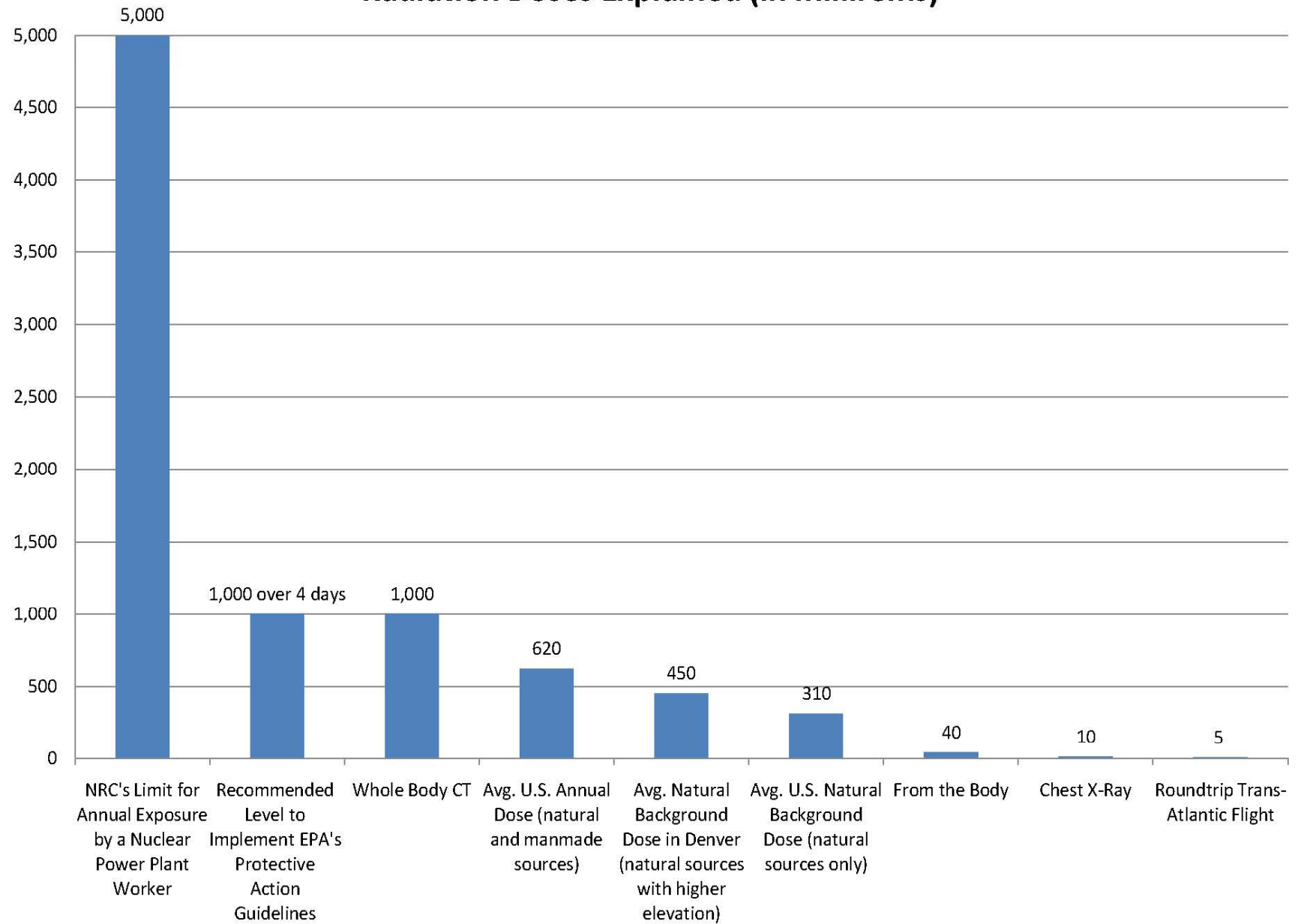
- Rapid decay of deposited radiological material indicating Radioiodine is the most significant component of dose
- Radiation levels consistently below actionable levels for evacuation or relocation outside of 25 miles; and levels continue to decrease
- No measurable deposit of radiological material since March 19
- US bases and facilities all measure dose rates below 32 microrem/hr (32 millionths of a REM) – a level with no known health risks
- Agricultural monitoring and possible intervention will be required for several hundred square kilometers surrounding the site:
  - Soil and water samples are the only definitive method to determine agricultural countermeasures
  - Ground monitoring can give better fidelity to identify areas that require agricultural sampling



# Context

- The Nuclear Regulatory Commission estimates that the average American absorbs 620 mRem a year\* (or 0.071 mRem/hour)
- An average transatlantic flight produces an exposure of 2.5 mRem\*
- A typical chest x-ray produces 10 mRem per image
- EPA guidelines call for public health actions if exposure exceeds 1000 mRem over 4 days
- Source: NRC: <http://nrc.gov/images/about-nrc/radiation/factoid2-lrg.gif>

## Radiation Doses Explained (in millirems)

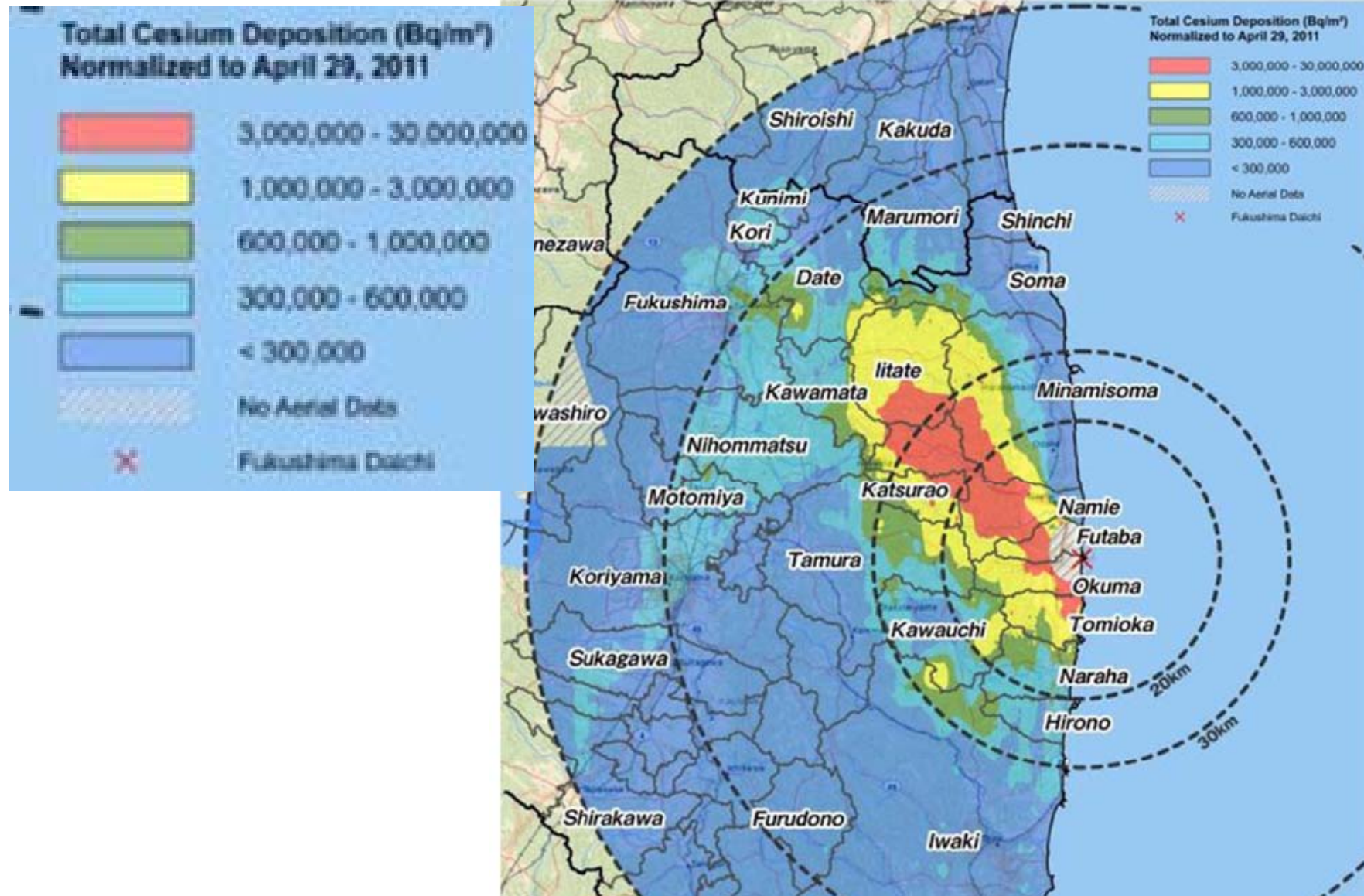




<http://www.iaea.org/newscenter/news/tsunamiupdate01.html>

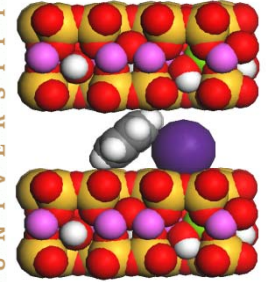
## Aerial Measuring Results

Joint US / Japan Survey Data



# Projected dose map

PURDUE  
UNIVERSITY



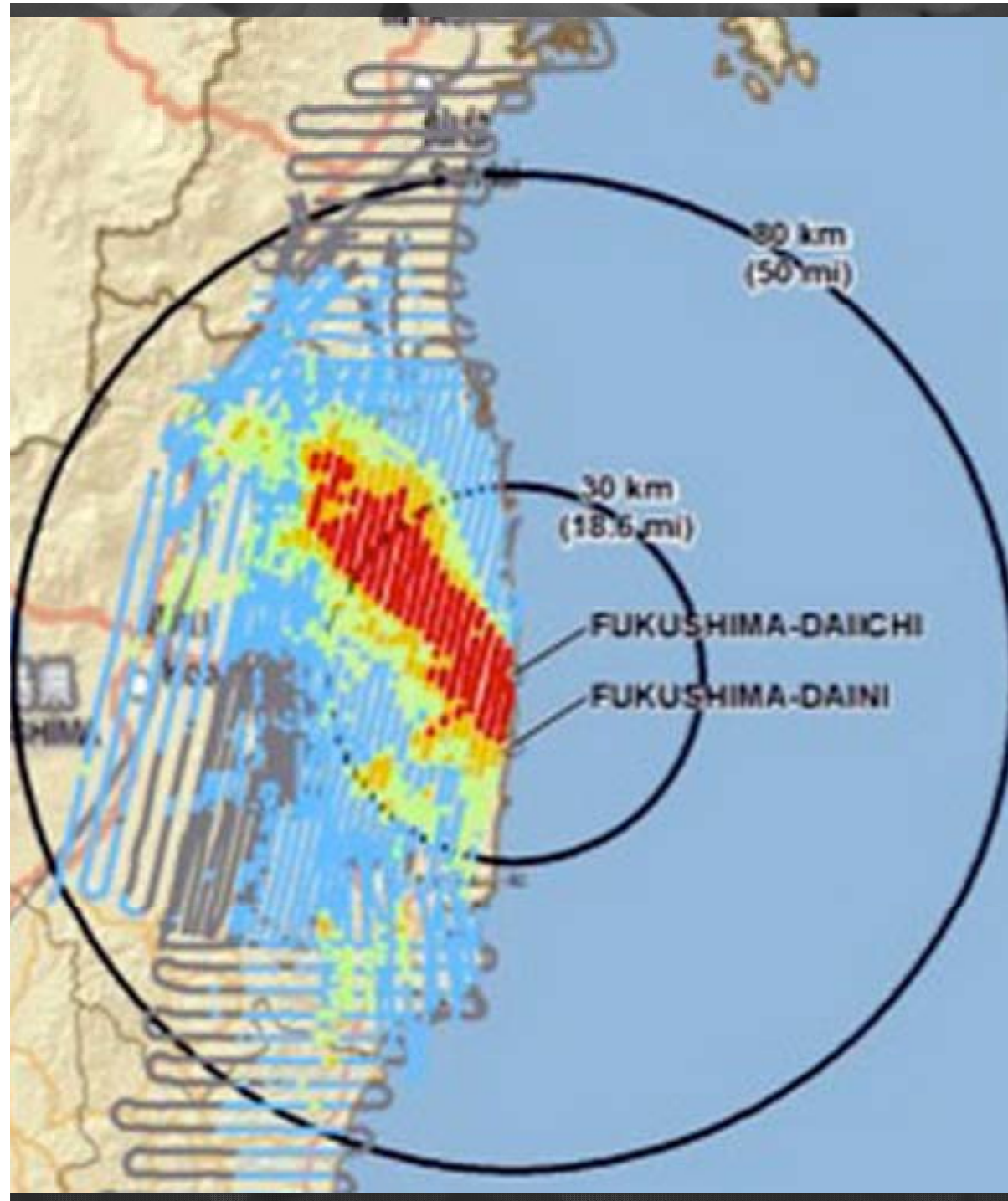
- Dust carried I-129 would dominate in first few months,
- Followed by Cs-137 on dust
- Followed by direct shine from outdoor exposure.
- Soil (and dust) is the primary source term



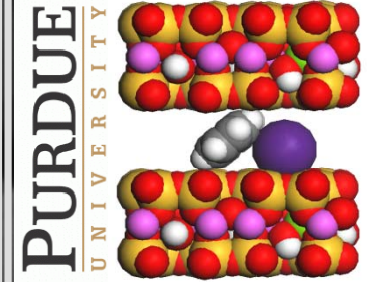
### Estimated First Year Dose

(mrem)

- > 2000
- 1000 - 2000
- 500 - 1000
- 100 - 500
- < 100



# Fukushima contamination comparison

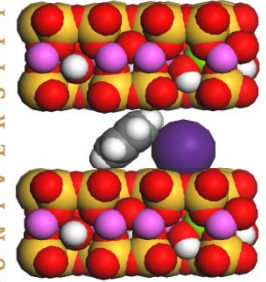


- At first, shine comes from everywhere.
- In Chernobyl, the roads became clear after a while and so only the bare soil areas show contamination now.
- There are areas on Earth where natural background radiation far exceed the Fukushima contamination.
- Example: A monazite black sand beach in Guarapari Brazil results in about 400x average dose for people living there.



# $^{137}\text{Cs}$ in Soils: The Role of Clay Minerals

PURDUE  
UNIVERSITY



- Clay minerals (layer silicates; phyllosilicates)
  - Small particle size ( $< 2 \mu\text{m}$ )
  - High surface area (can exceed  $750 \text{ m}^2/\text{g}$ )
  - One of nature's most important nanomaterials
  - Clay minerals have a very high affinity of  $^{137}\text{Cs}$ .
  - Have overall negative charge
- Clay minerals control many aspects of the fate and transport of  $^{137}\text{Cs}$  in soils.
- Other phases may be important:
  - Carbonates and Soil Organic Matter

$^{137}\text{Cs}^+$

Charge = +1

Large size

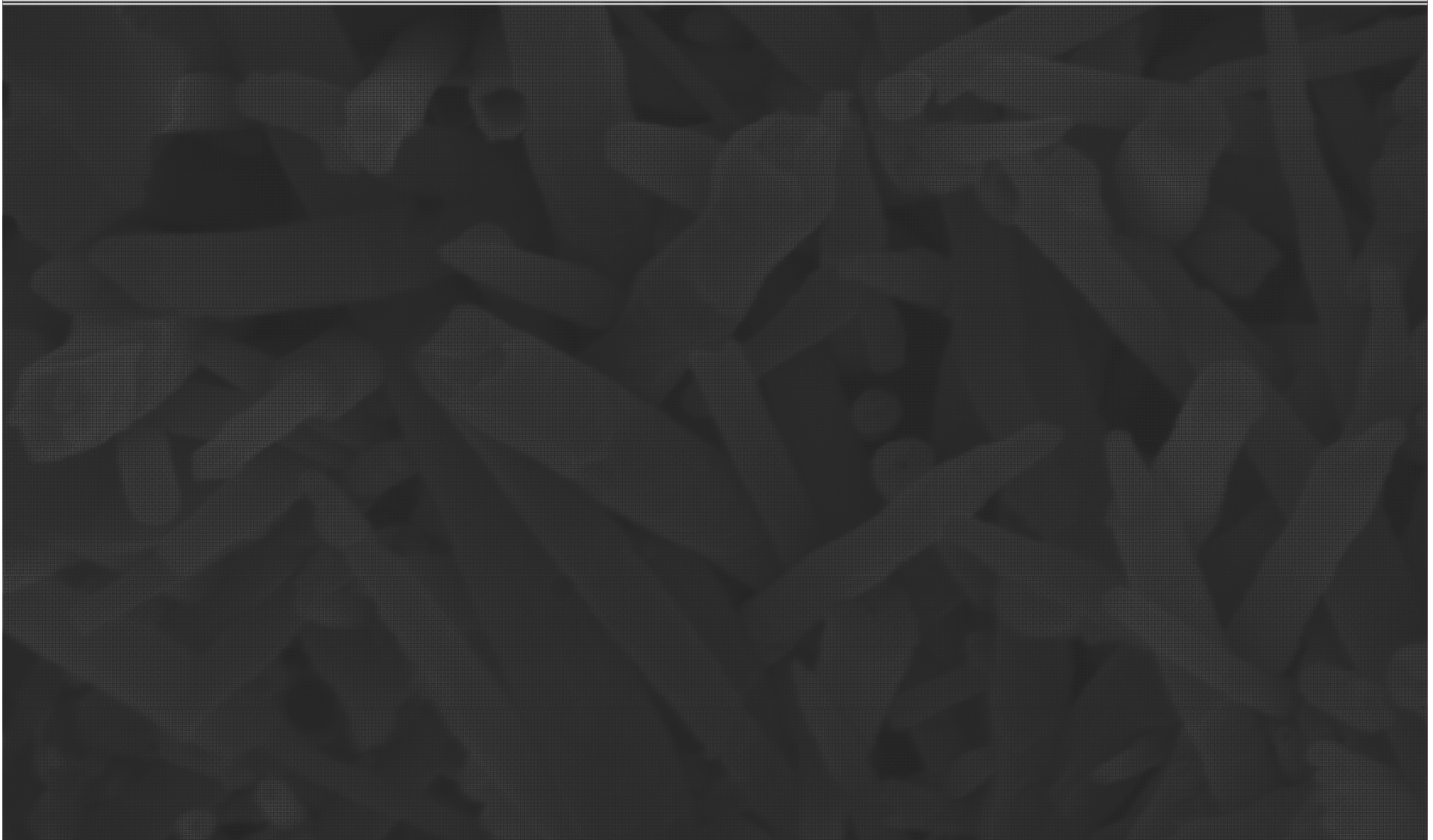
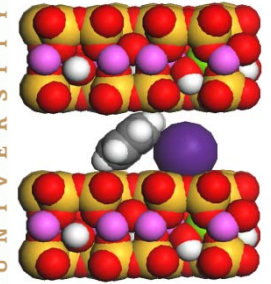
Low Enthalpy of hydration

Small hydrated radius



# Movement of $^{137}\text{Cs}$ in soils

PURDUE  
UNIVERSITY



# Heavy Metals in the Environment

## Storage and Migration of Fallout Strontium-90 and Cesium-137 for Over 40 Years in the Surface Soil of Nagasaki

Yasunori Mahara\*

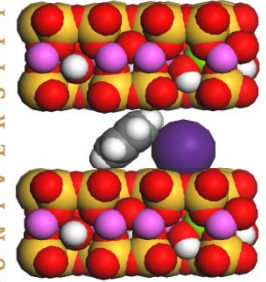
- Vertical migration of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  was investigated in an unsaturated soil layer in the Nishiyama area of Nagasaki.
- The in situ migration rates of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  were estimated to be 4.2 mm/yr and 1.0 mm/yr
- Fallout of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  have remained in the surface soil for a long period of time
- More than 95% of  $^{137}\text{Cs}$  was to a depth of 0.1 m, no  $^{137}\text{Cs}$  was detected in groundwater.
- $^{90}\text{Sr}$  was more mobile.

J. Environ. Qual. 22:722–730 (1993).



# Vertical migrations of $^{137}\text{Cs}$

PURDUE  
UNIVERSITY



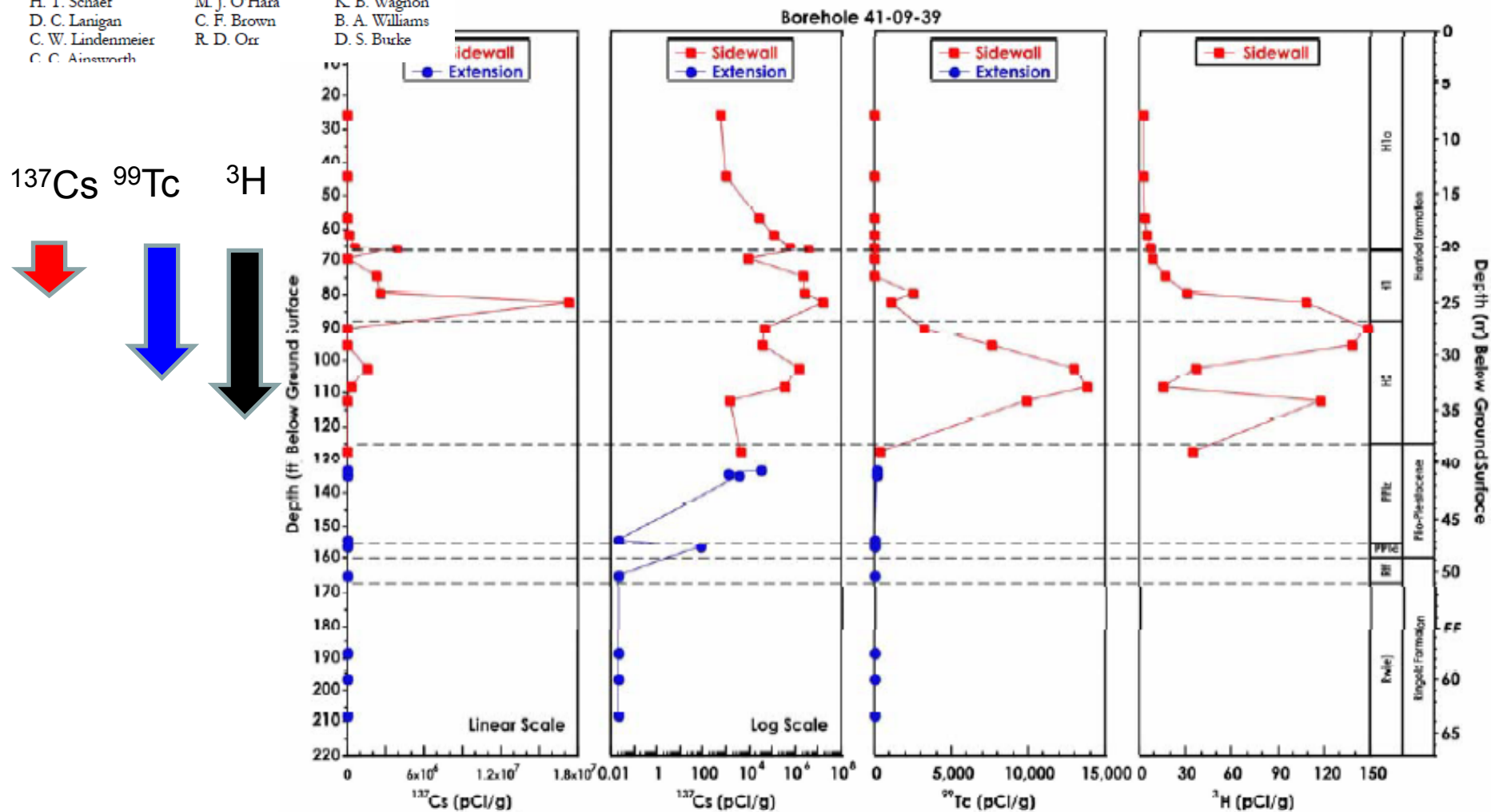
- Slow vertical movement of  $^{137}\text{Cs}$  in soils and sediments
- Next figure – compare  $^{137}\text{Cs}$  to  $^{99}\text{Tc}$  or  $^3\text{H}$

Characterization of Vadose Zone  
Sediment: Borehole 41-09-39  
in the S-SX Waste Management Area

R. J. Serne  
G. V. Last  
H. T. Schaefer  
D. C. Lanigan  
C. W. Lindenmeier  
C. C. Ainsworth

R. E. Clayton  
V. L. LeGore  
M. J. O'Hara  
C. F. Brown  
R. D. Orr

I. V. Kutnyakov  
T. C. Wilson  
K. B. Wagnon  
B. A. Williams  
D. S. Burke



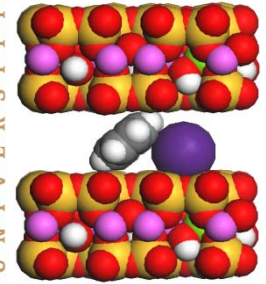
2002/UC2/41-09-39/020

Figure 5.3. Cesium-137, Technetium-99, Strontium-90, and Tritium in Sediments from Table 5.11 Versus Depth with Geology Breaks

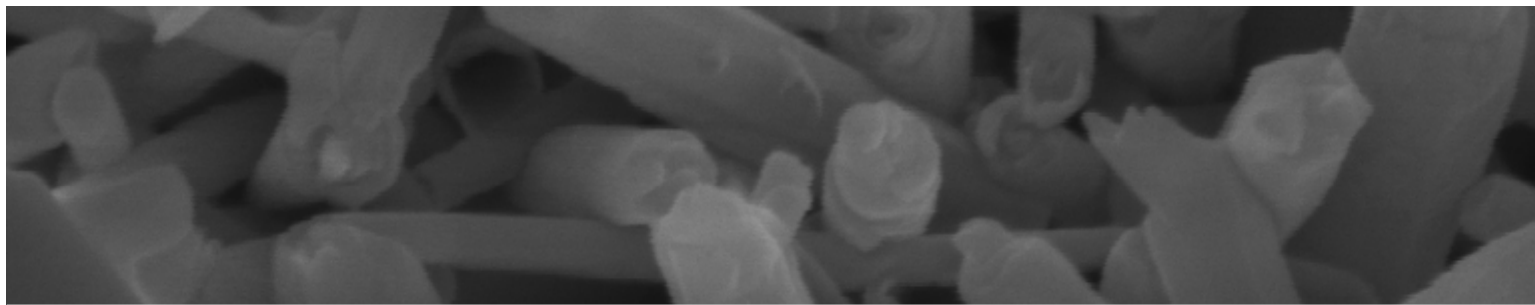


# General Behavior of $^{137}\text{Cs}$ in soils

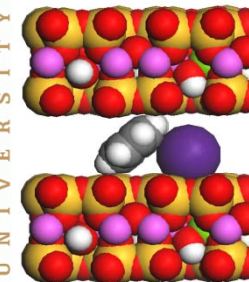
PURDUE  
UNIVERSITY



- High selectivity
- Sorption models
- Kinetics



PURDUE  
UNIVERSITY



*Clays and Clay Minerals*, Vol. 33, No. 3, 251–257, 1985.

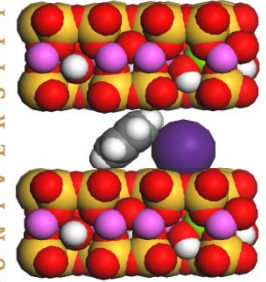
## FORMATION OF HIGHLY SELECTIVE CESIUM-EXCHANGE SITES IN MONTMORILLONITES

ANDRÉ MAES, DIRK VERHEYDEN, AND ADRIEN CREMERS

Research has shown that a small fraction of the 'active sites' on clay mineral have a very high affinity for  $^{137}\text{Cs}$



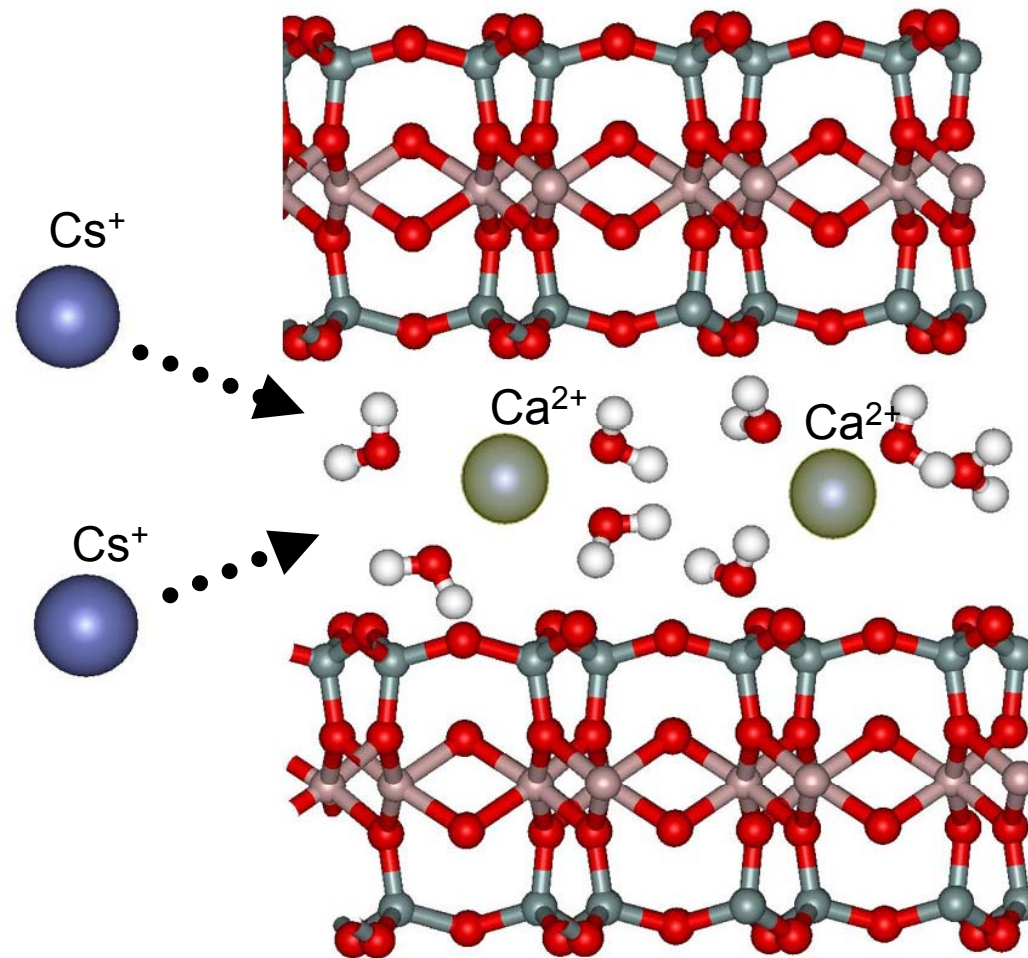
# Ion Exchange



- Ion Exchange
- $2 \text{Cs}^+ + \text{CaX}_2 = 2\text{CsX} + \text{Ca}^{2+}$

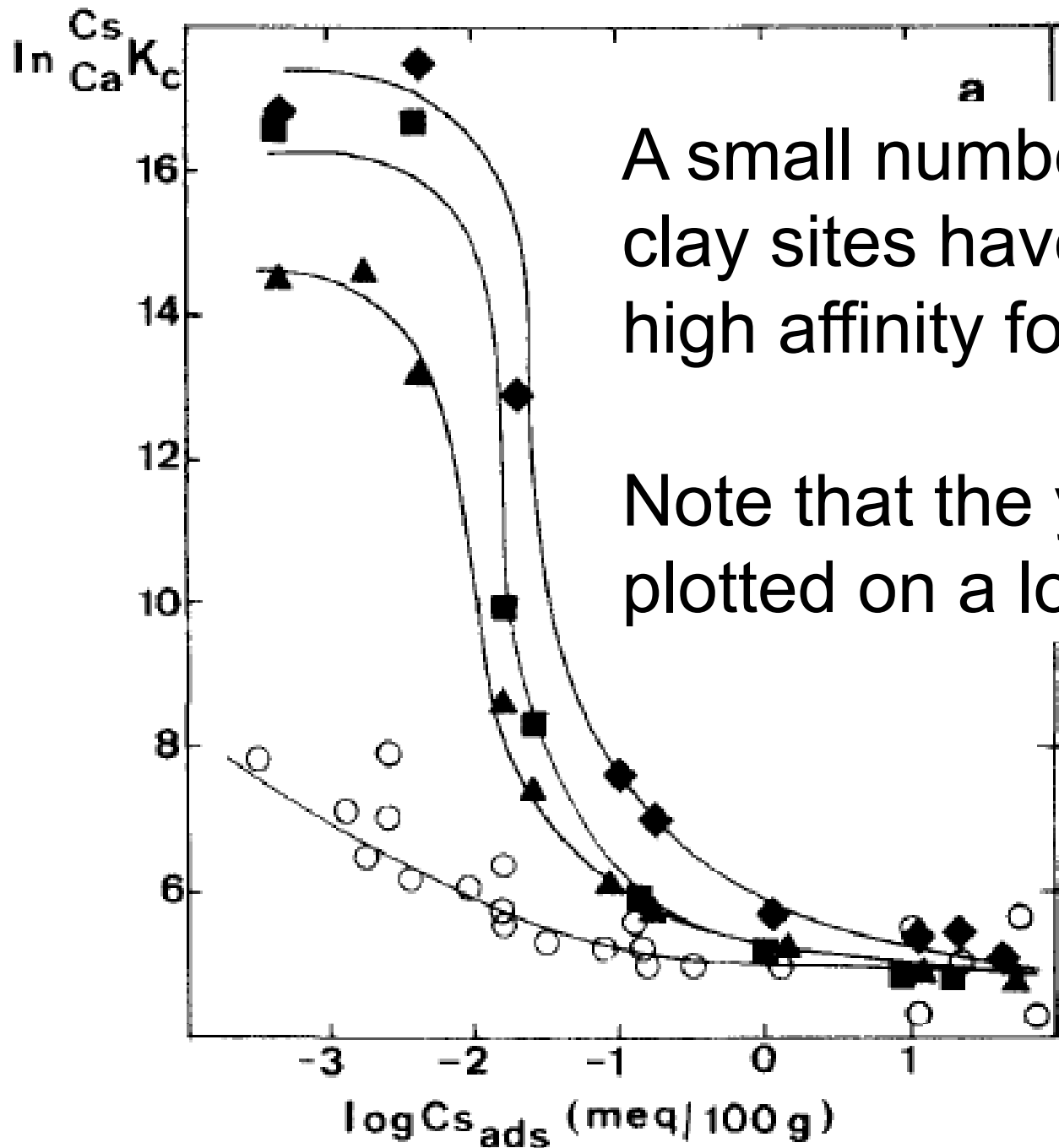
$$K_c = \frac{\{\text{CsX}\}^2 (\text{Ca}^{2+})}{\{\text{CaX}_2\} (\text{Cs}^+)^2}$$

# Cation exchange of $\text{Ca}^{2+}$ by $\text{Cs}^{+}$



Johnston et al., Langmuir 17(12) 3712-3718

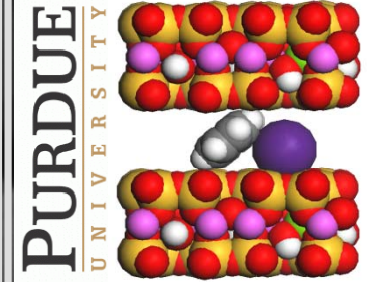




A small number of clay sites have a very high affinity for Cs

Note that the y-axis is plotted on a log scale!

## Main point



- Some sites on clay matrices have a very high affinity for  $\text{Cs}^+$ .
- However, these sites are very limited.
- The highest energy sites have a  $\text{Ln } K_c$  of 33.8 ( $\Delta G_{\text{exchange}} = 40 \text{ kJ/mol}$ )
- But represent only a very trace fraction of the total sites:
  - 0.0002% of total sites!



# **FREUNDLICH AND DUAL LANGMUIR ISOTHERM MODELS FOR PREDICTING $^{137}\text{Cs}$ BINDING ON SAVANNAH RIVER SITE SOILS**

Momoko Goto,\* Robert Rosson,<sup>†</sup> J. Marion Wampler,<sup>‡</sup> W. Crawford Elliott,<sup>§</sup>  
Steven Serkiz,\*\* and Bernd Kahn<sup>†</sup>

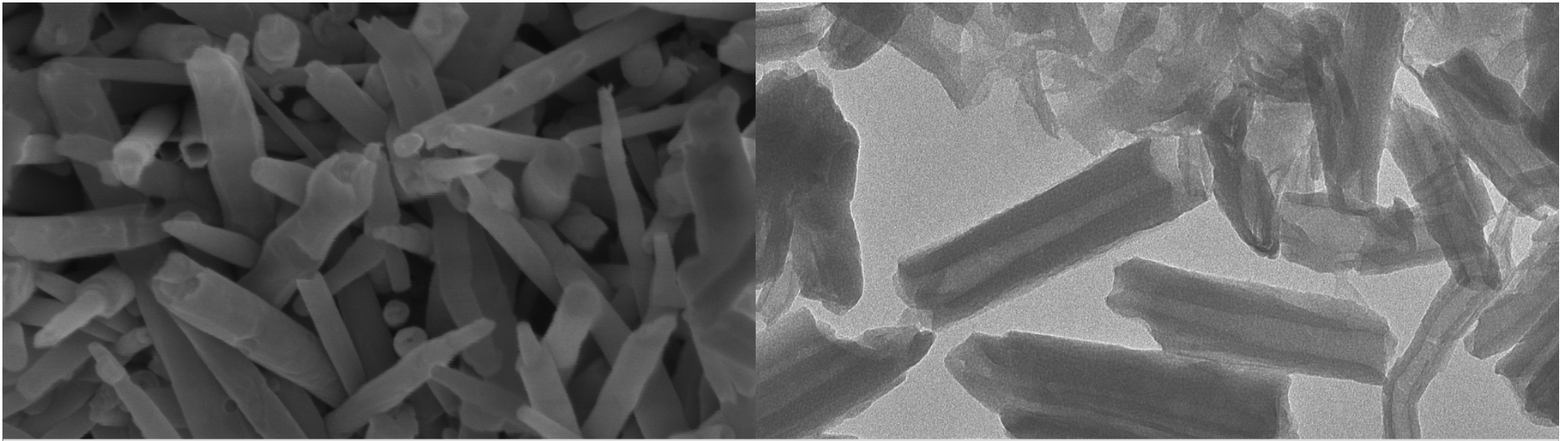
Health Physics

January 2008, Volume 94, Number 1

Soil sample	Added cesium <sup>a</sup> ( $\mu\text{eq}$ )	<sup>137</sup> Cs		$K_d^c$ (L kg <sup>-1</sup> )
		In solution (kBq L <sup>-1</sup> )	On soil <sup>b</sup> (kBq kg <sup>-1</sup> )	
Fuquay	$1.24 \times 10^{-3}$	0.250	352	$1,410 \pm 60$
	$3.75 \times 10^{-1}$	0.810	330	$410 \pm 10$
	$1.78 \times 10^0$	1.05	314	$300 \pm 10$
Orangeburg	$1.24 \times 10^{-3}$	0.136	350	$2,570 \pm 100$
		0.169	340	$2,010 \pm 90$
	$3.75 \times 10^{-1}$	1.17	311	$270 \pm 10$
		1.02	311	$300 \pm 10$
Blanton	$1.24 \times 10^{-3}$	0.533	332	$620 \pm 20$
	$7.25 \times 10^{-2}$	2.82	248	$88 \pm 4$
	$3.75 \times 10^{-1}$	3.51	220	$63 \pm 3$
	$1.24 \times 10^{-3}$	0.831	325	$390 \pm 20$
Vaucluse		1.09	314	$290 \pm 10$
	$7.25 \times 10^{-2}$	2.73	250	$92 \pm 4$
		2.83	250	$89 \pm 4$
	$3.75 \times 10^{-1}$	4.02	199	$50 \pm 3$
		4.01	197	$49 \pm 3$

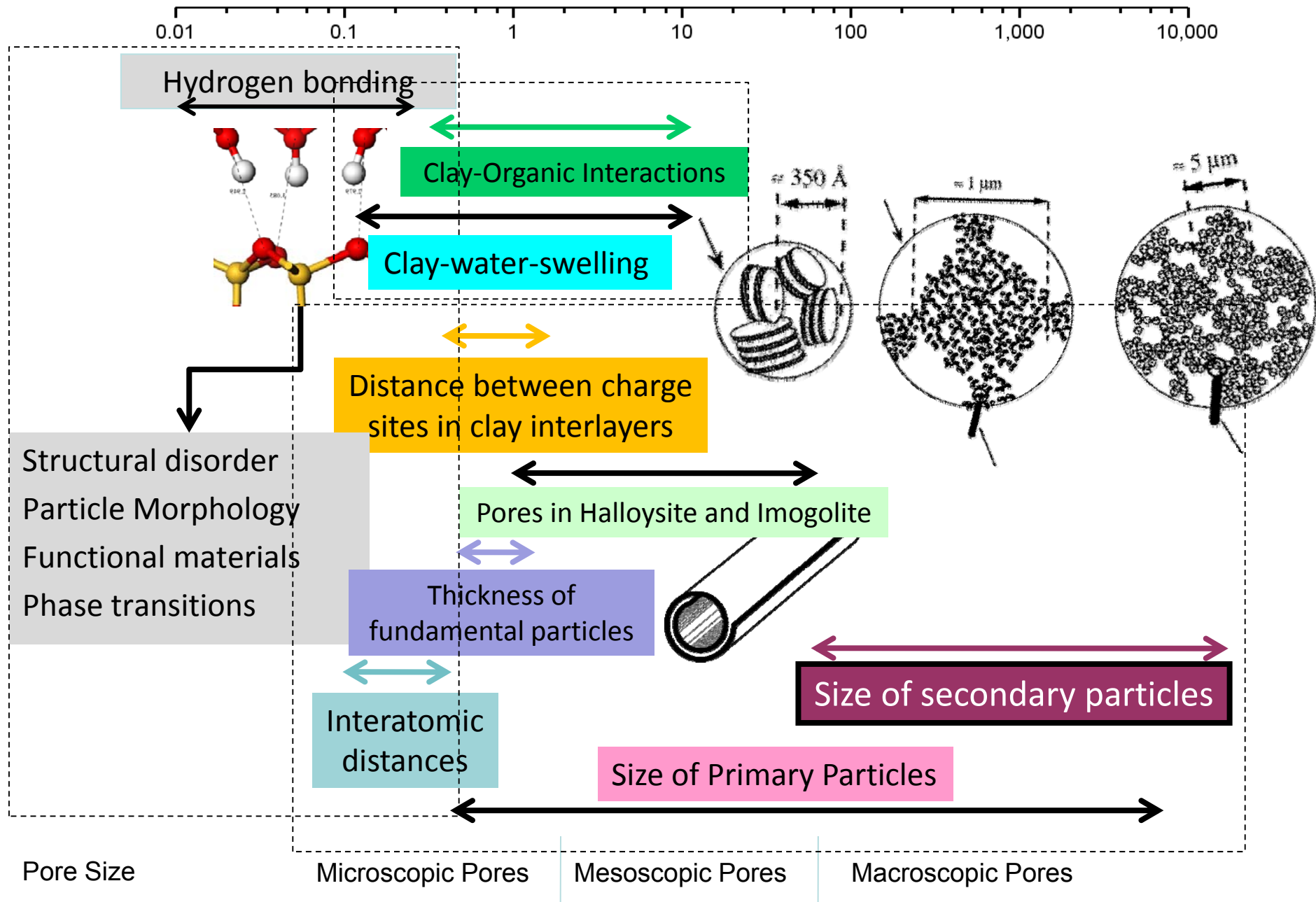
High  $K_d$  value means that Cs is partitioned into the soil.



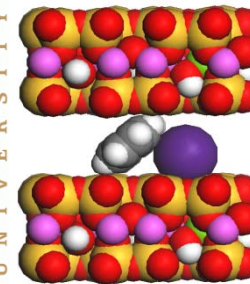


# Introduction to the nanoscale architecture of clay<sup>v</sup> minerals

(length scale of nanometers)





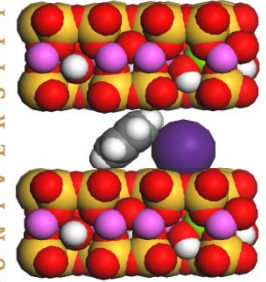


How does  $^{137}\text{Cs}^+$  bind to clay particles?



J. P. McKinley et al., *Environ. Sci. Technol.*  
35 (17):3433-3441, 2001.

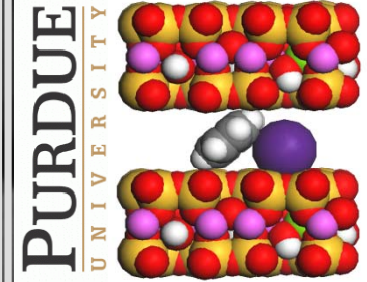
PURDUE  
UNIVERSITY



- The retention of  $^{137}\text{Cs}^+$  by sediments and phyllosilicates has been intensively studied since anthropogenic  $^{137}\text{Cs}^+$  became a concern for environmental and health reasons .
- Sorption and desorption were observed to proceed in two steps:
  - rapid initial reaction
  - followed by slower continued reaction (or even renewed sorption, in the case of desorption).

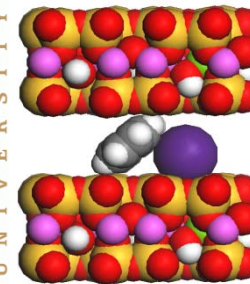


## Proposed model. Three different chemical surface sites:



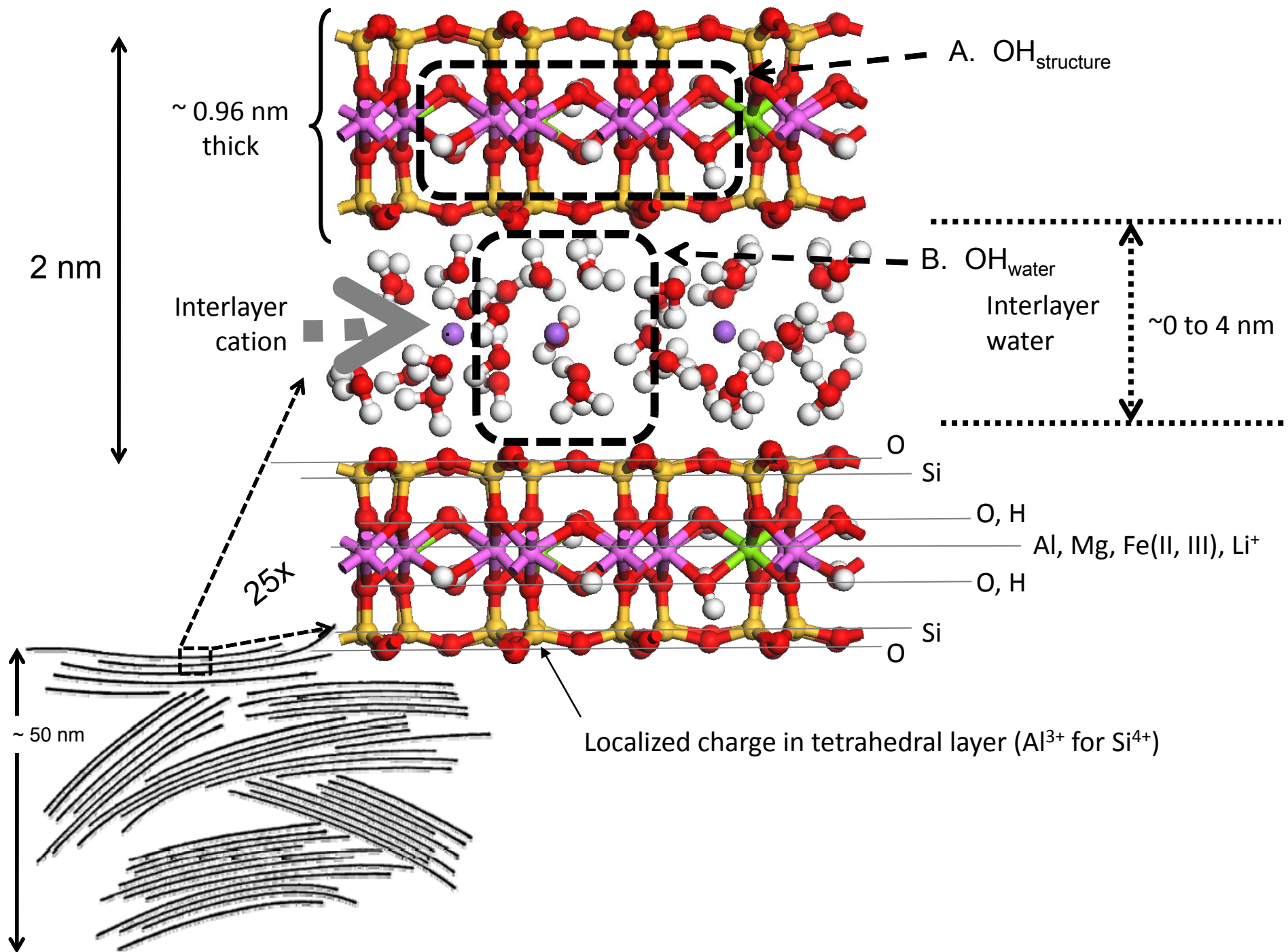
- Nonselective (fixed charge) exchange sites on phyllosilicate surfaces;
- Selective frayed edge sites (FES) on micas, formed by the removal of  $K^+$  from the phyllosilicate interlayers
- Interlayer sites in micas, populated by the diffusion of  $^{137}\text{Cs}$  from FES.



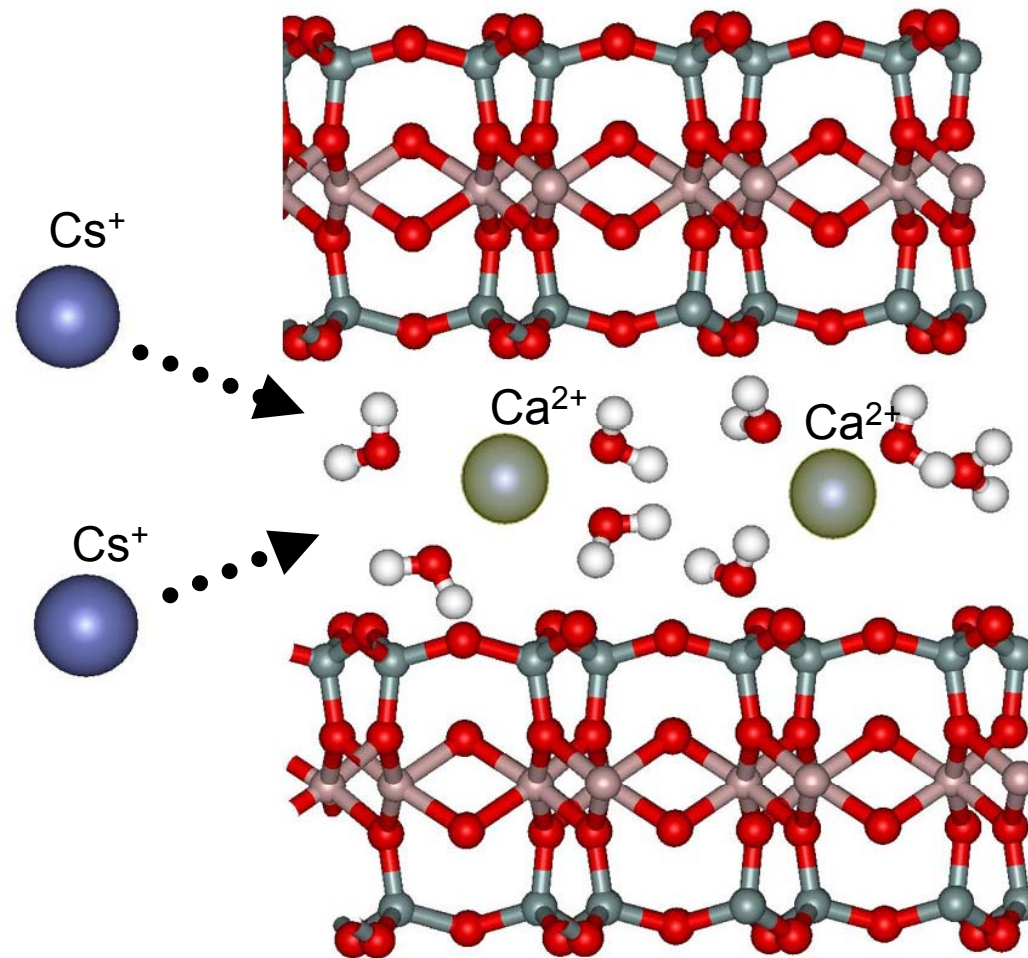


Nonselective exchange sites





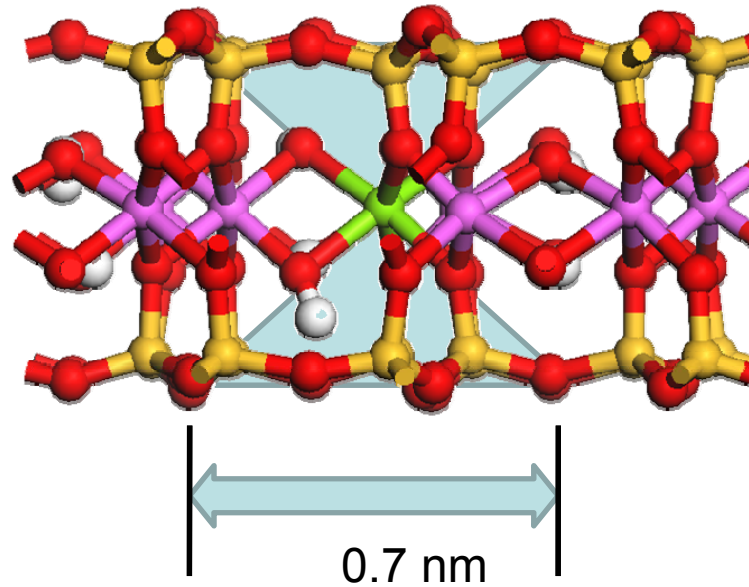
# Cation exchange of $\text{Ca}^{2+}$ by $\text{Cs}^+$



Johnston et al., Langmuir 17(12) 3712-3718



Isomorphous Substitution of  $\text{Mg} \rightarrow \text{Al}$  in the octahedral layer  
(montmorillonite)



Isomorphous Substitution of  $\text{Al} \rightarrow \text{Si}$  in the tetrahedral layer  
(saponite)

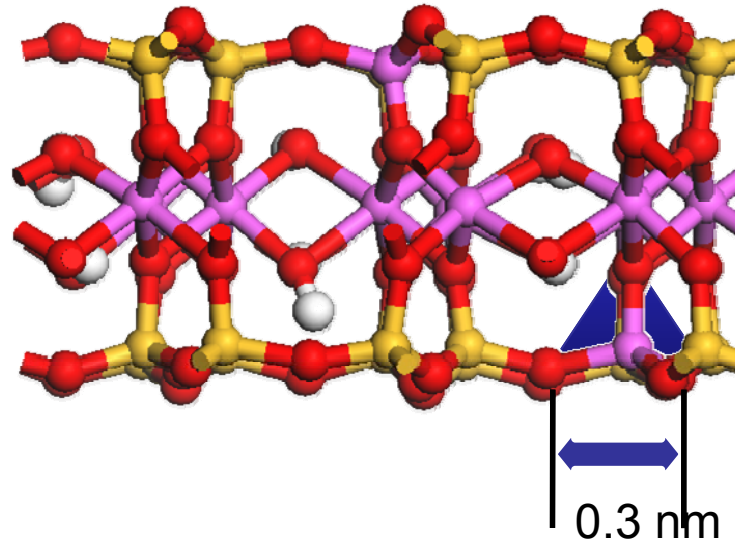
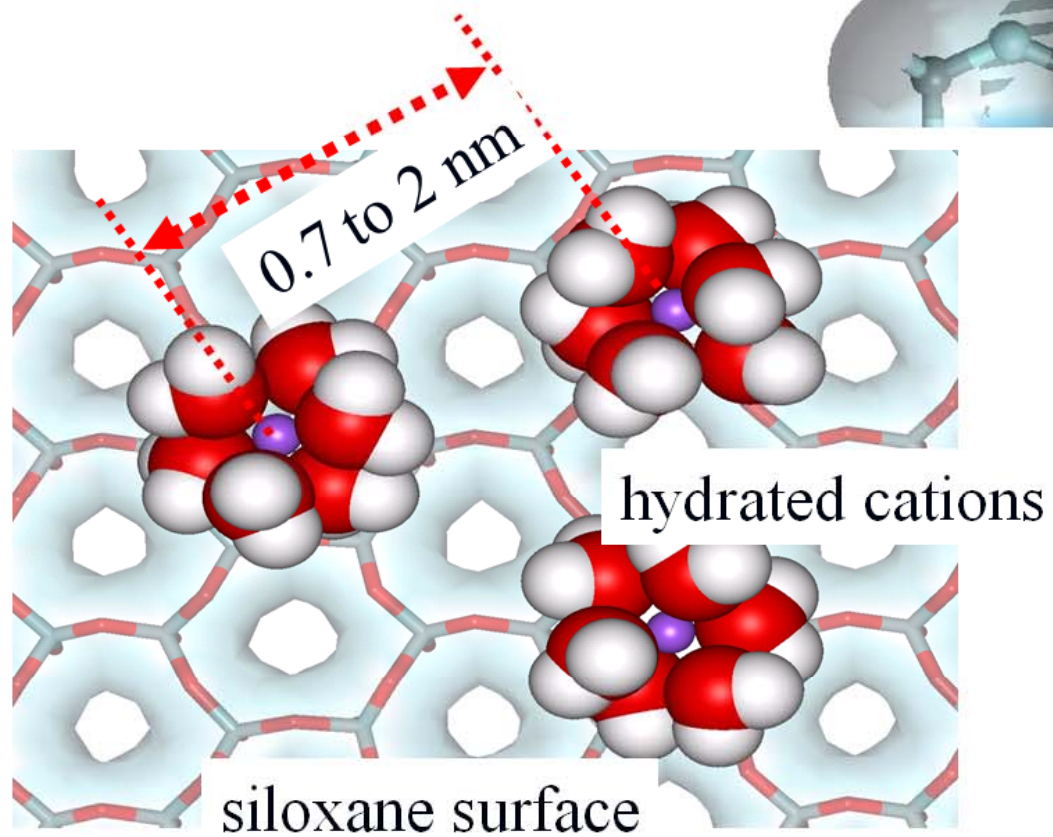
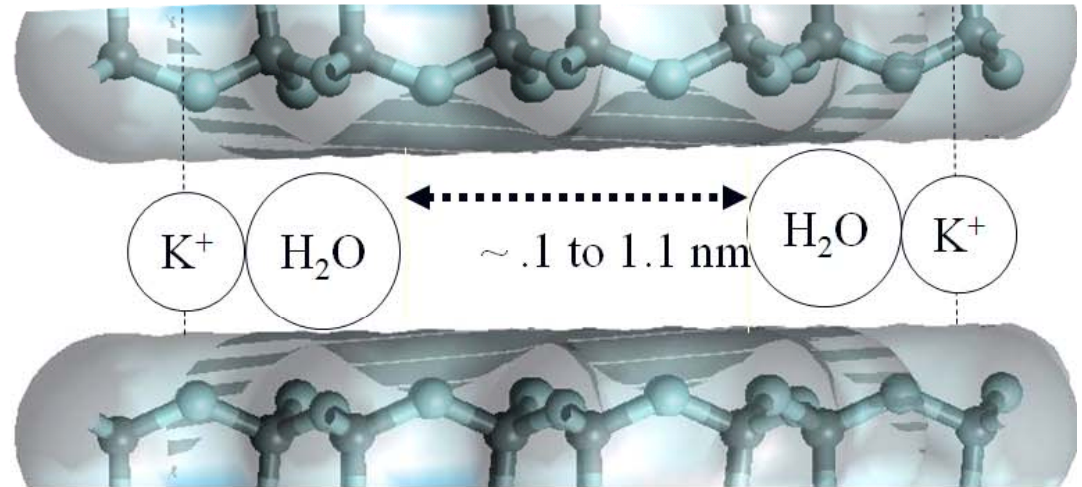


Figure 8

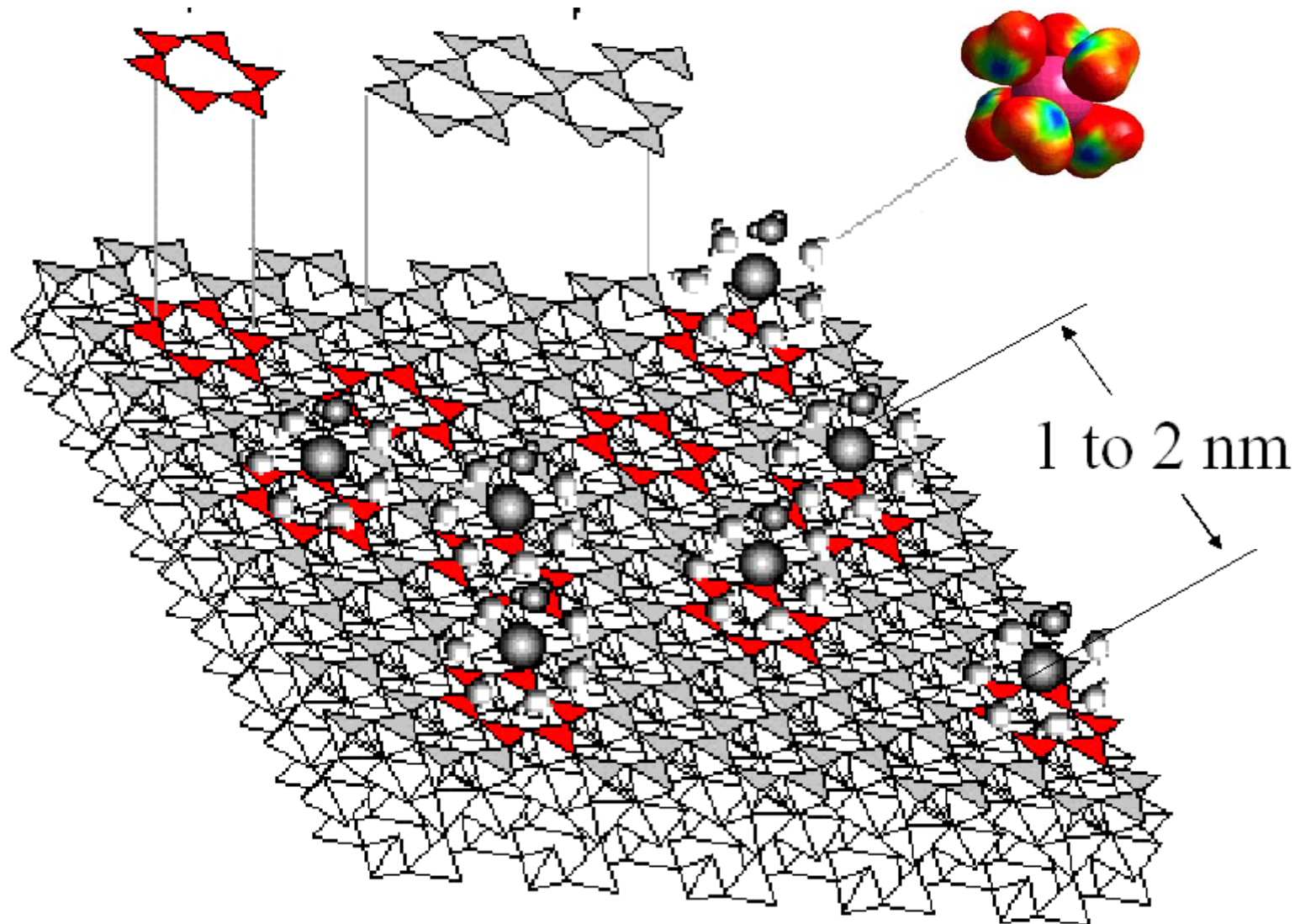
1 to 2 nm  
Neutral siloxane surface 0.1 to 1.1 nm

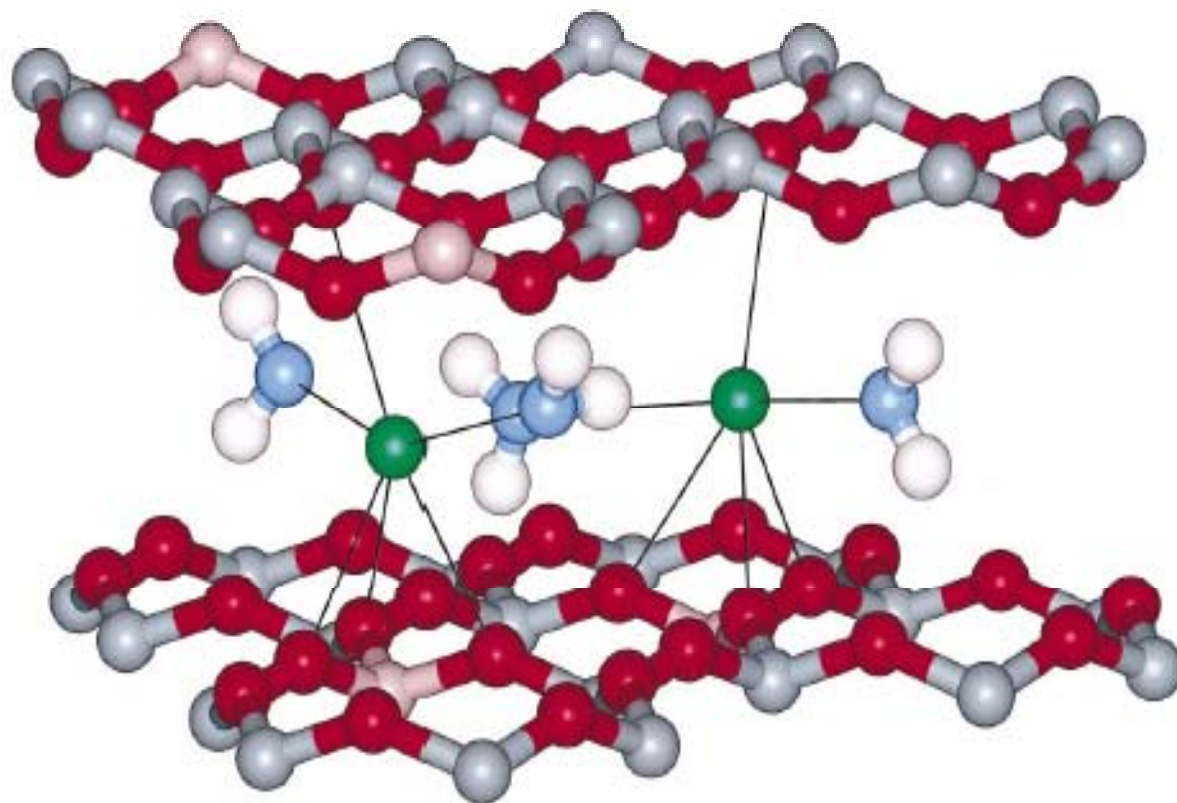
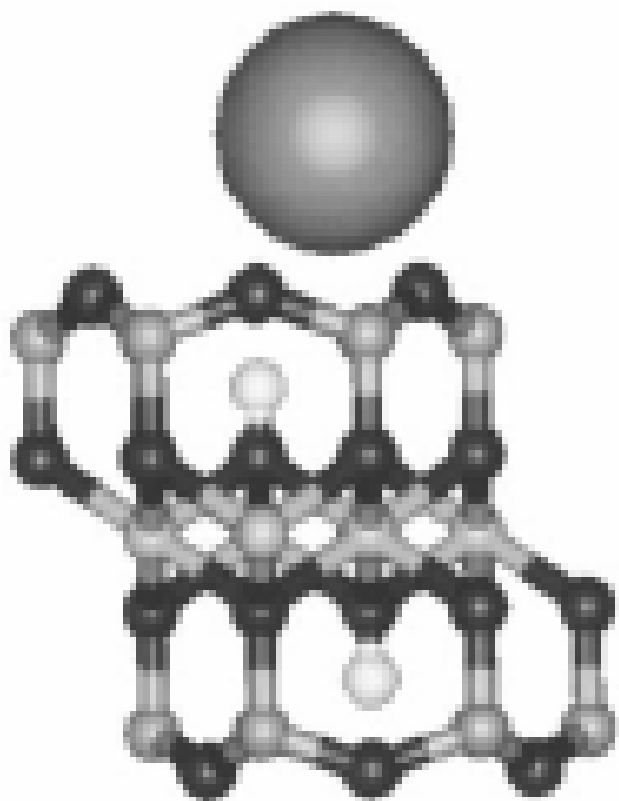




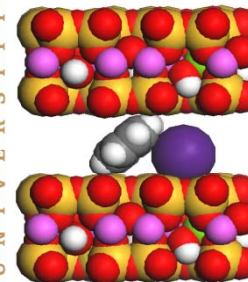
Hydrophilic Sites  
(red)

Hydrophobic sites  
(grey)



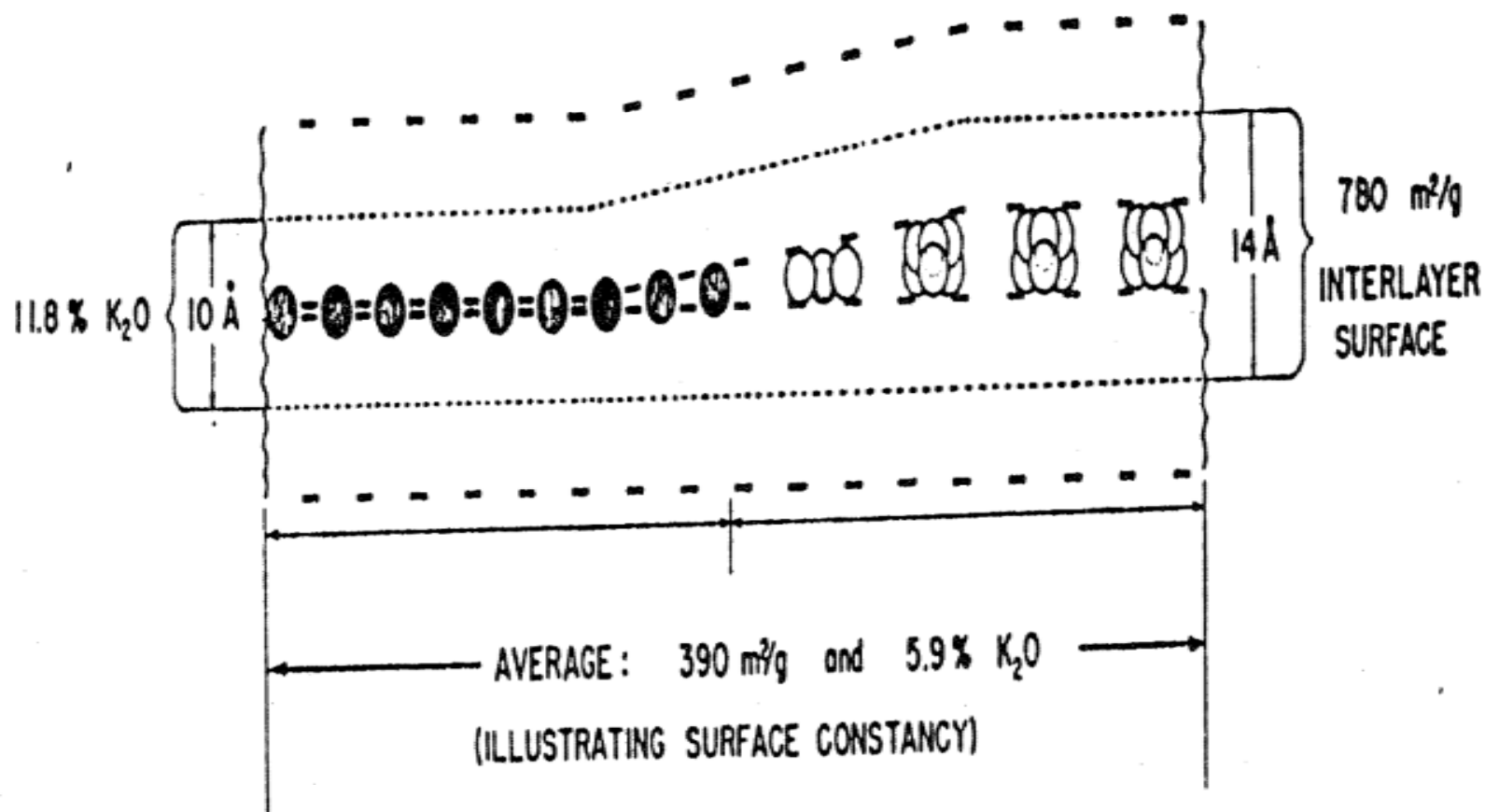
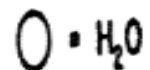






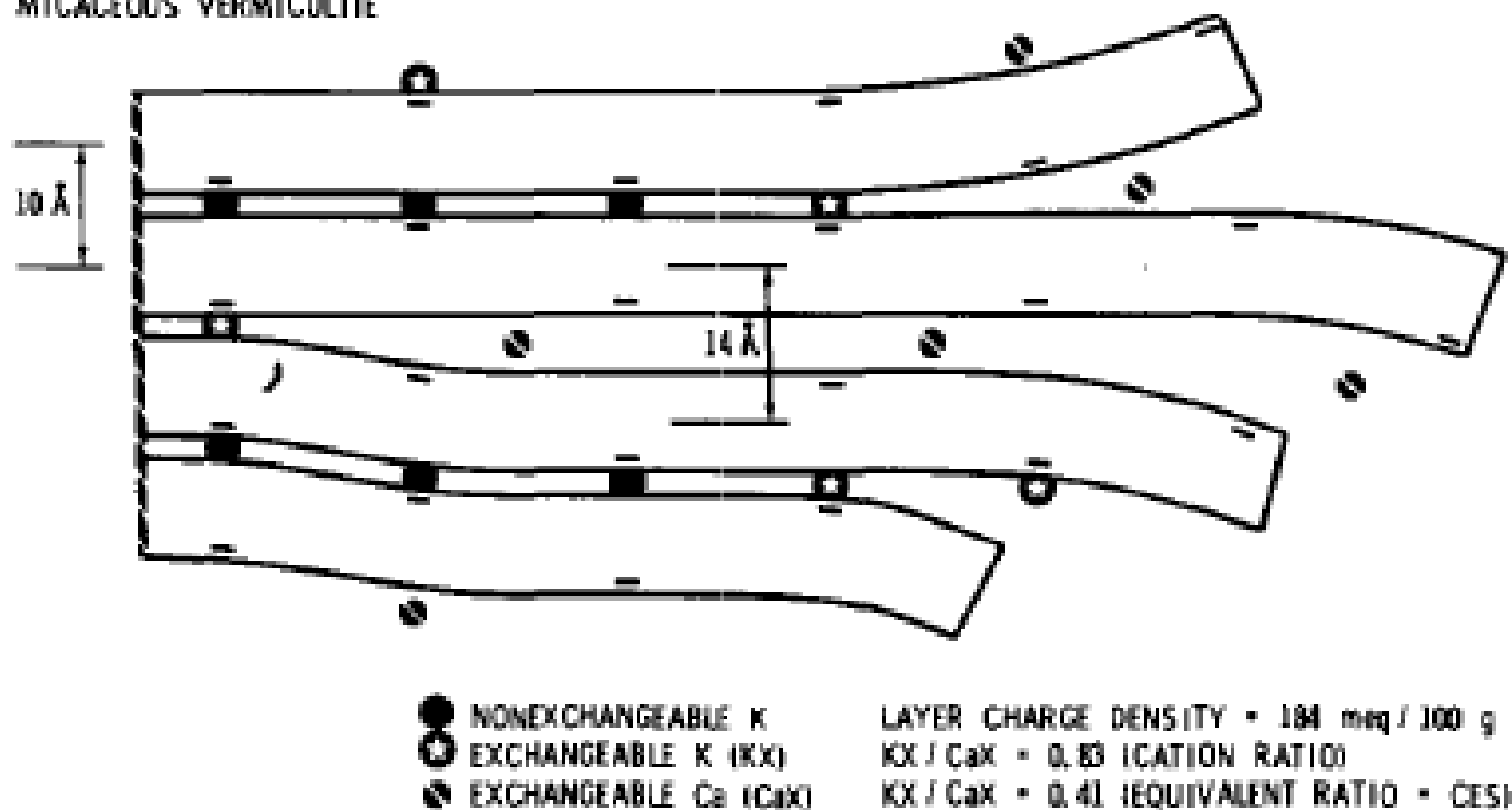
# Selective frayed edge sites (FES) on micas

# MICA CLEAVAGE AT "FRAYED EDGE"





# MICACEOUS VERMICULITE



## Cation Exchange Selectivity of Some Clay-Sized Minerals and Soil Materials<sup>1</sup>

D. L. DOLCATER, E. G. LOTSE, J. K. SYERS, AND M. L. JACKSON<sup>2</sup> SOIL SCI. SOC. AMER. PROC., VOL. 32, 1968

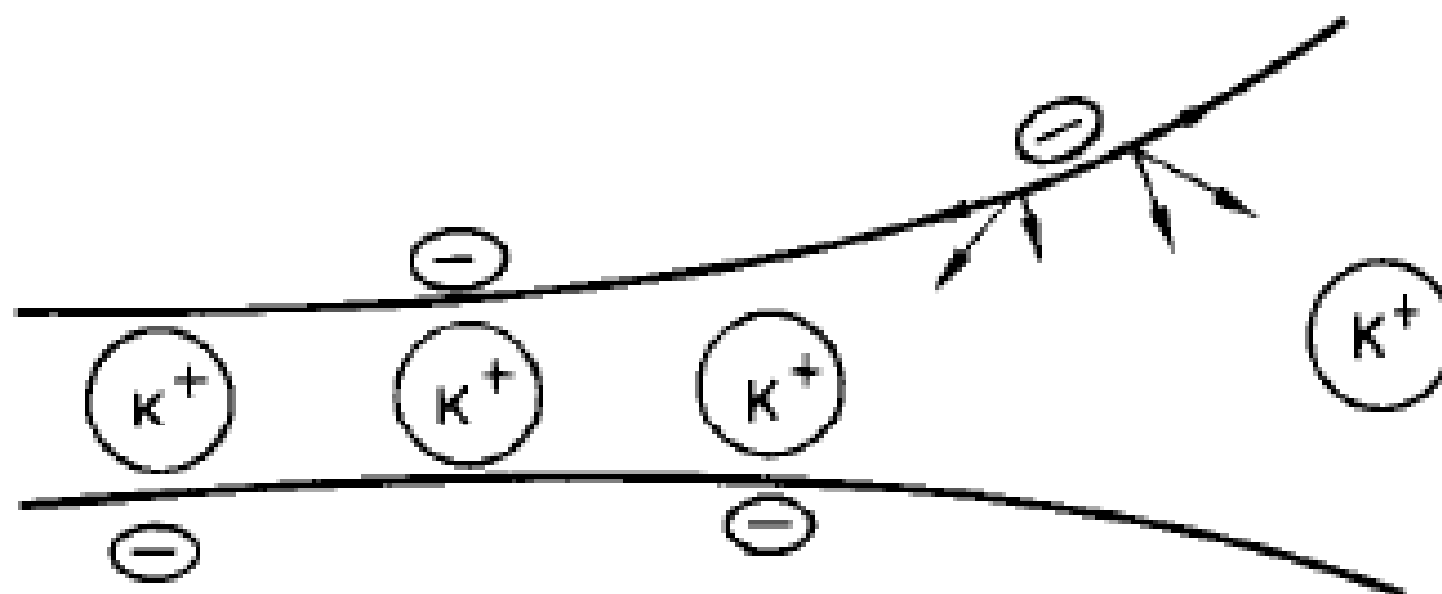
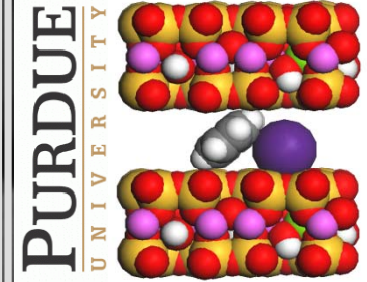


Fig. 1. Selective sorption of a  $K^+$  ion in a frayed edge of a weathered mica sheet.



# Sorption behavior linked to specific exchange sites:

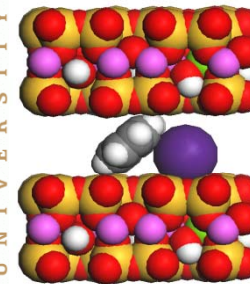


- Nonselective exchange sites weakly retained  $^{137}\text{Cs}^+$ , which could be readily and rapidly desorbed.
- The FES sites rapidly and energetically retained  $\text{Cs}^+$  and also slowly desorbed  $\text{Cs}^+$ ,
- In most experimental studies, complete recovery of sorbed  $\text{Cs}^+$  was not achievable, and this unrecovered  $\text{Cs}^+$  was considered to be “irreversibly sorbed” or “fixed”.



# Kinetics of Cs exchange

PURDUE  
UNIVERSITY



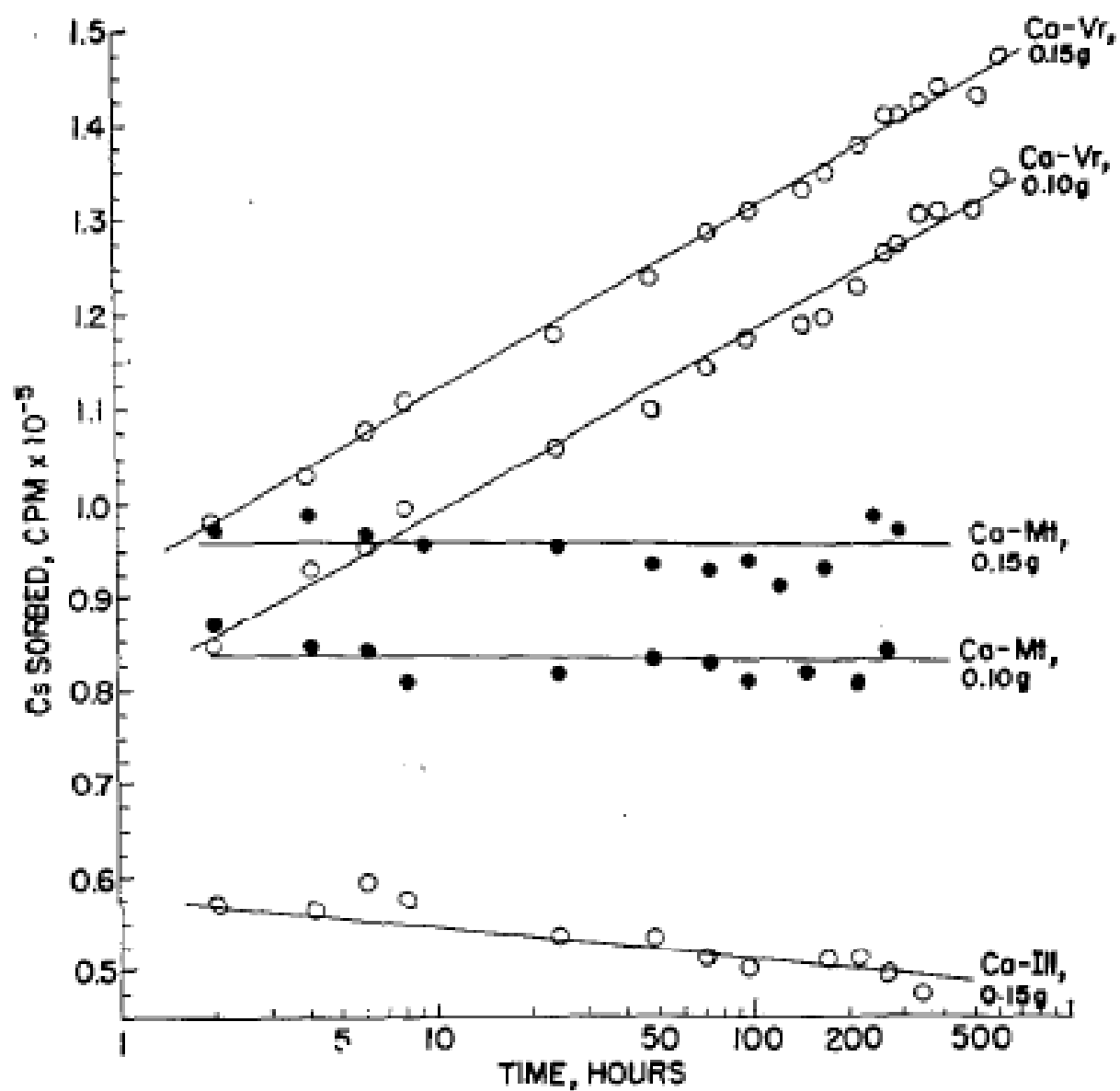


Fig. 1—Sorption of Cs by Ca-saturated clay minerals with time.  
Il = illite, Mt = montmorillonite, Vr = vermiculite.



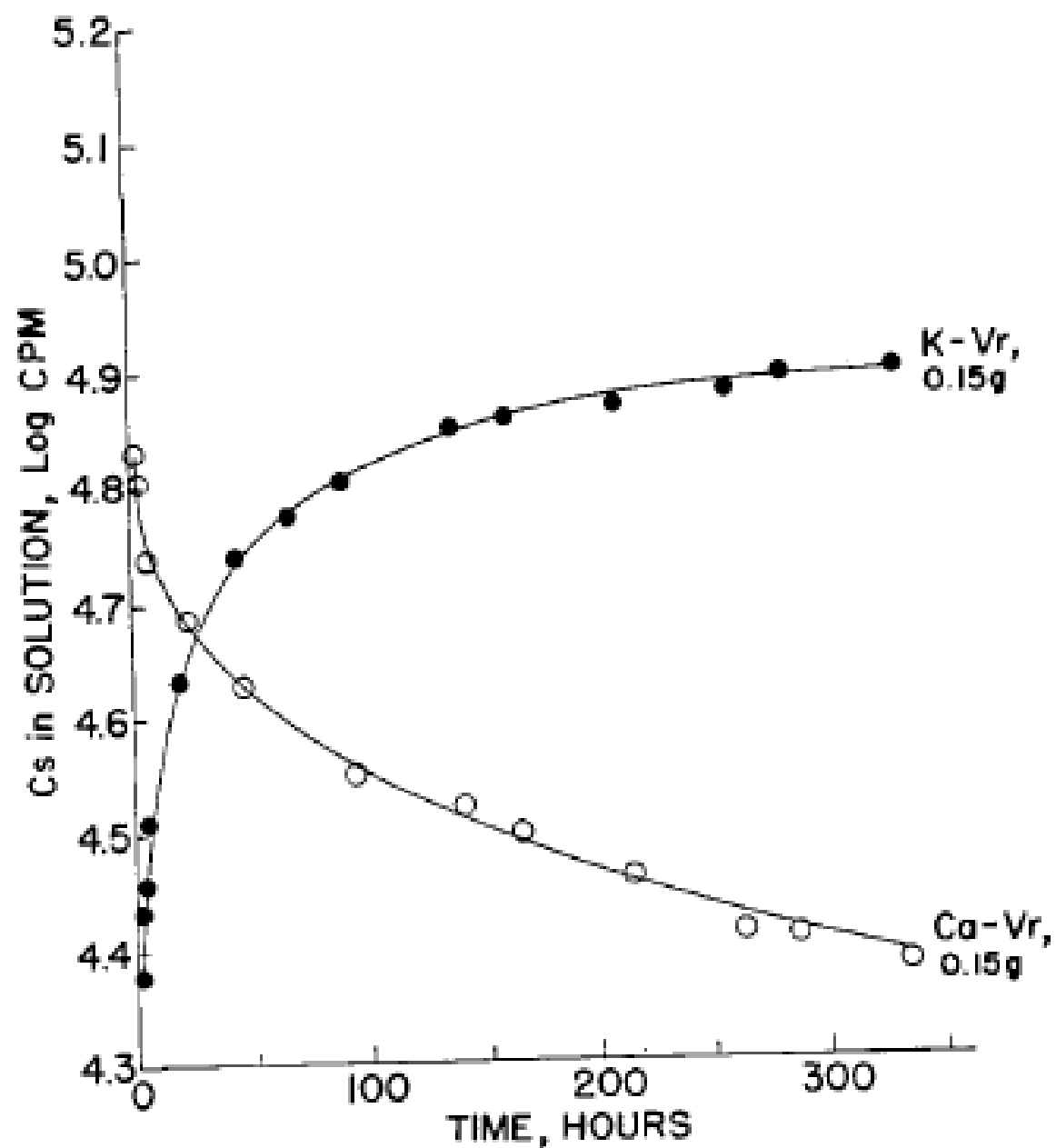
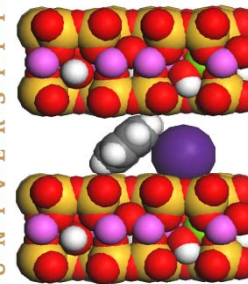
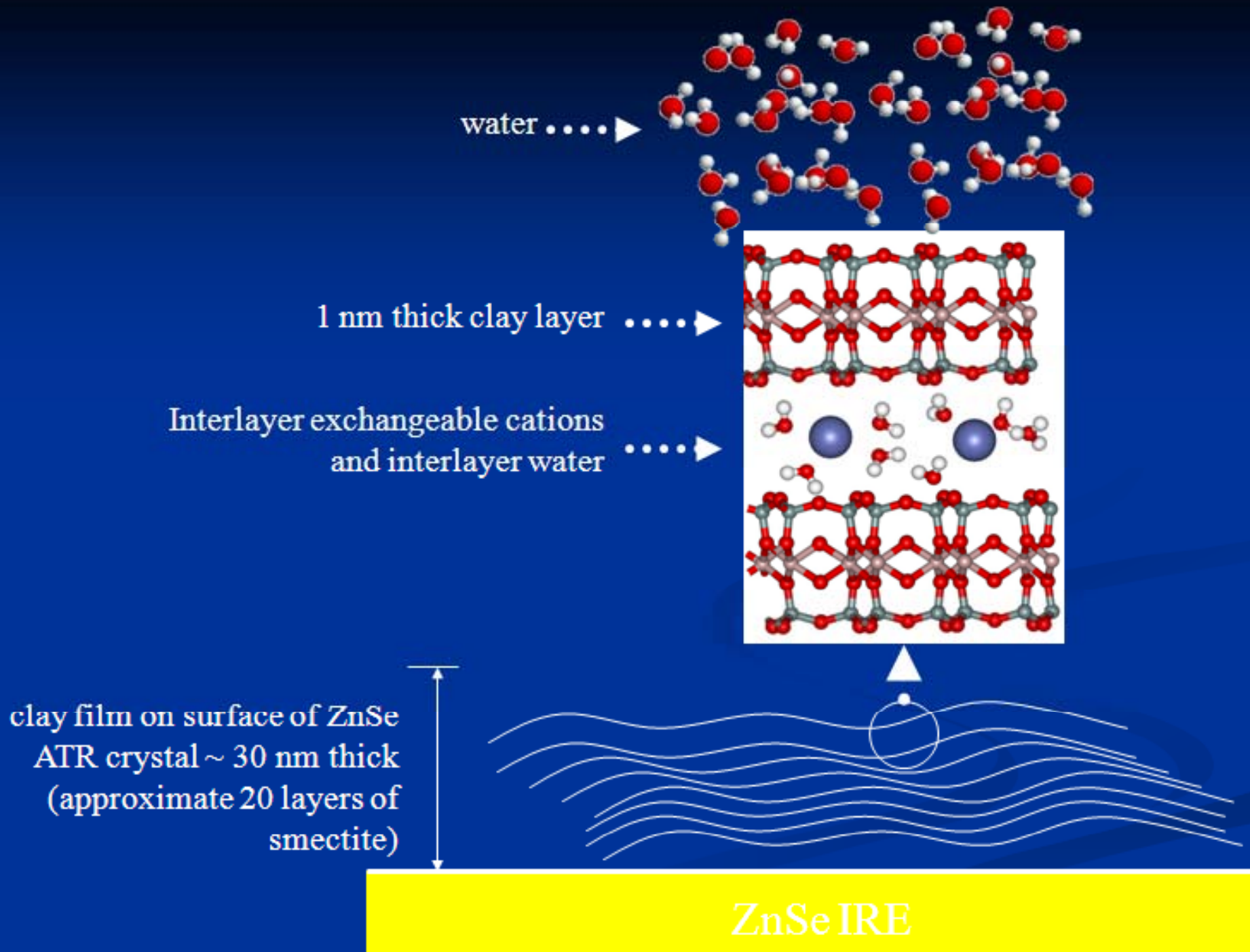


Fig. 5—Diffusion of Cs into Ca-saturated vermiculite and its release from K-saturated vermiculite.

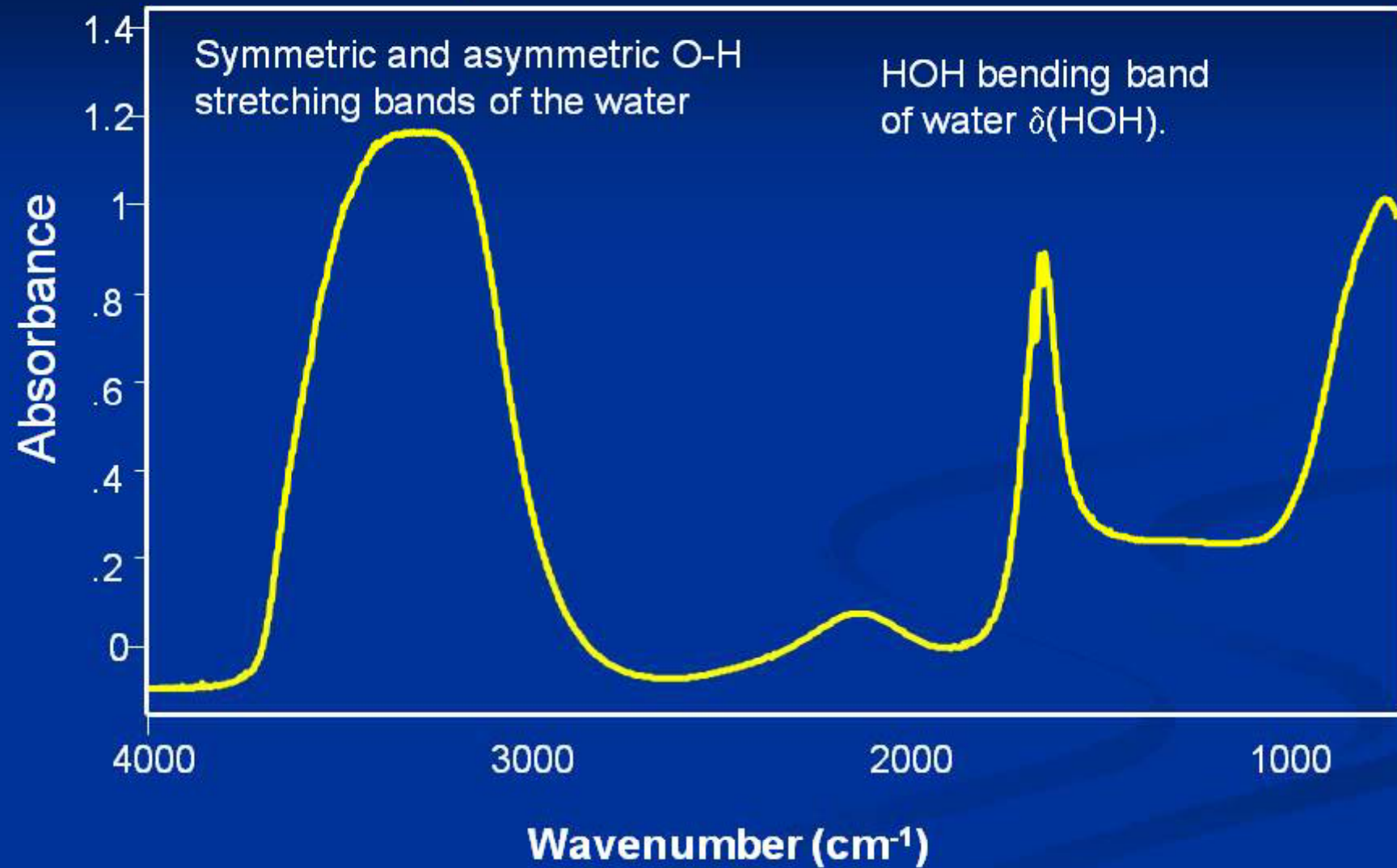


# Molecular Interactions of $^{137}\text{Cs}^+$ with Clay Minerals

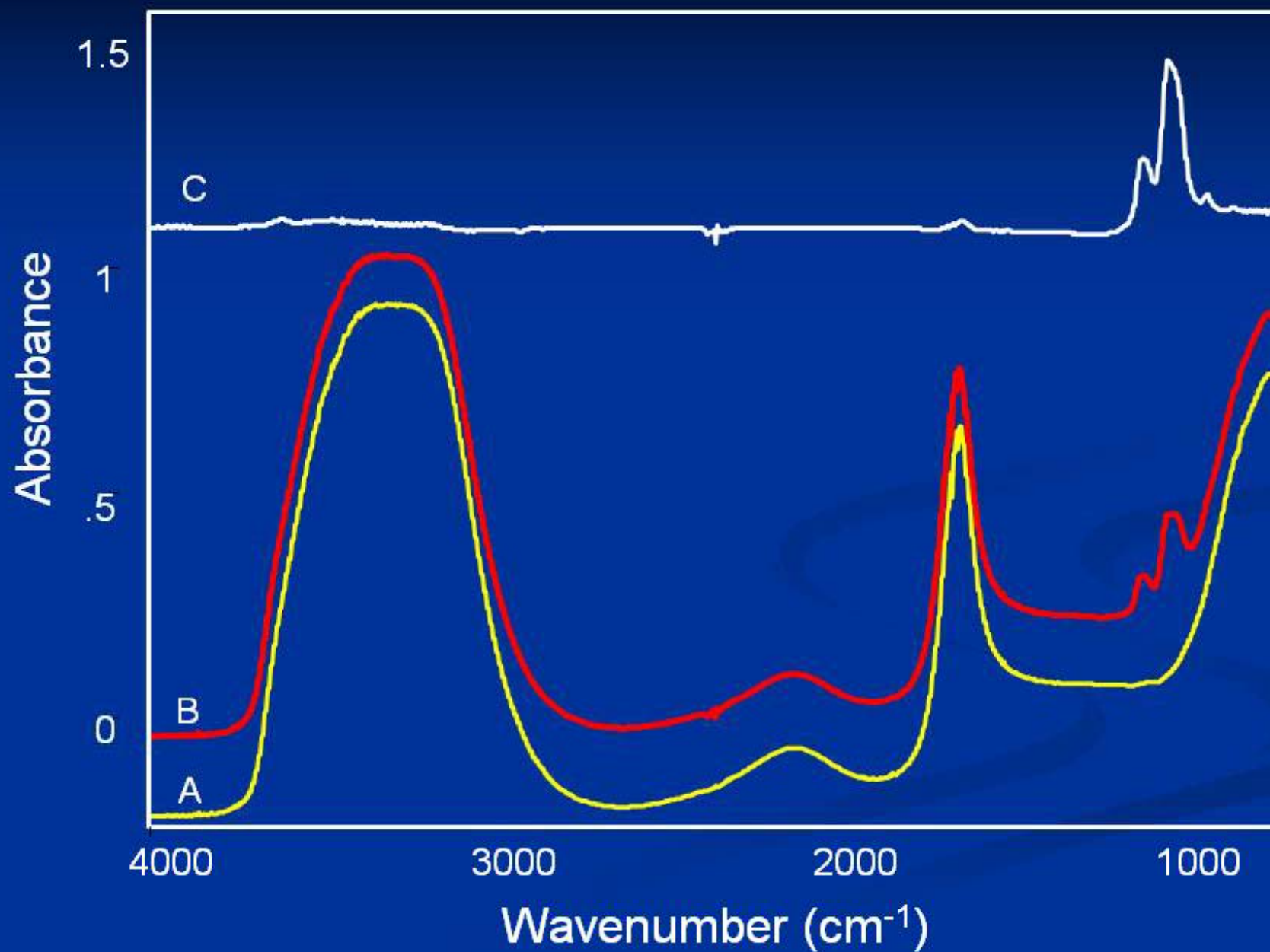




# ATR-FTIR Spectrum of water



## ATR-FTIR Spectrum of smectite in aqueous suspension



# FTIR Study of Mg $\rightarrow$ Na exchange

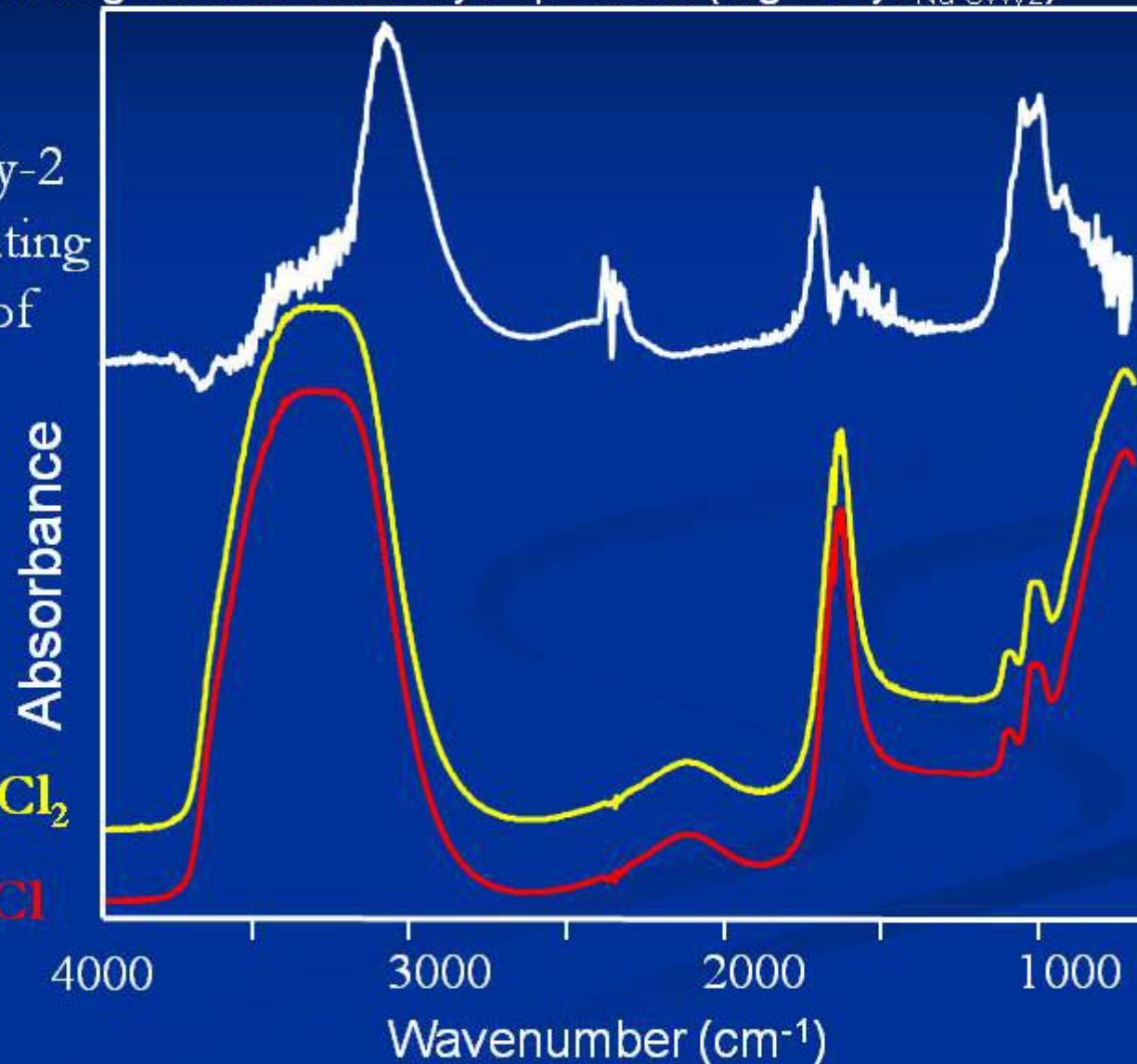
The white spectrum is the **S**ubtractively **N**ormalized **I**nterfacial FTIR (FTIR) spectrum of Mg-Wy2 ratioed against the Na-SWy2 spectrum (Mg-SWy2<sub>Na-SWy2</sub>)

$$\mathbf{C} = \mathbf{B} - \mathbf{A}$$

Mg-SWy-2 – Na-SWy-2  
Spectral changes resulting  
from the exchange of  
Mg<sup>2+</sup> for Na<sup>+</sup>

**B:** clay + 0.1 M MgCl<sub>2</sub>

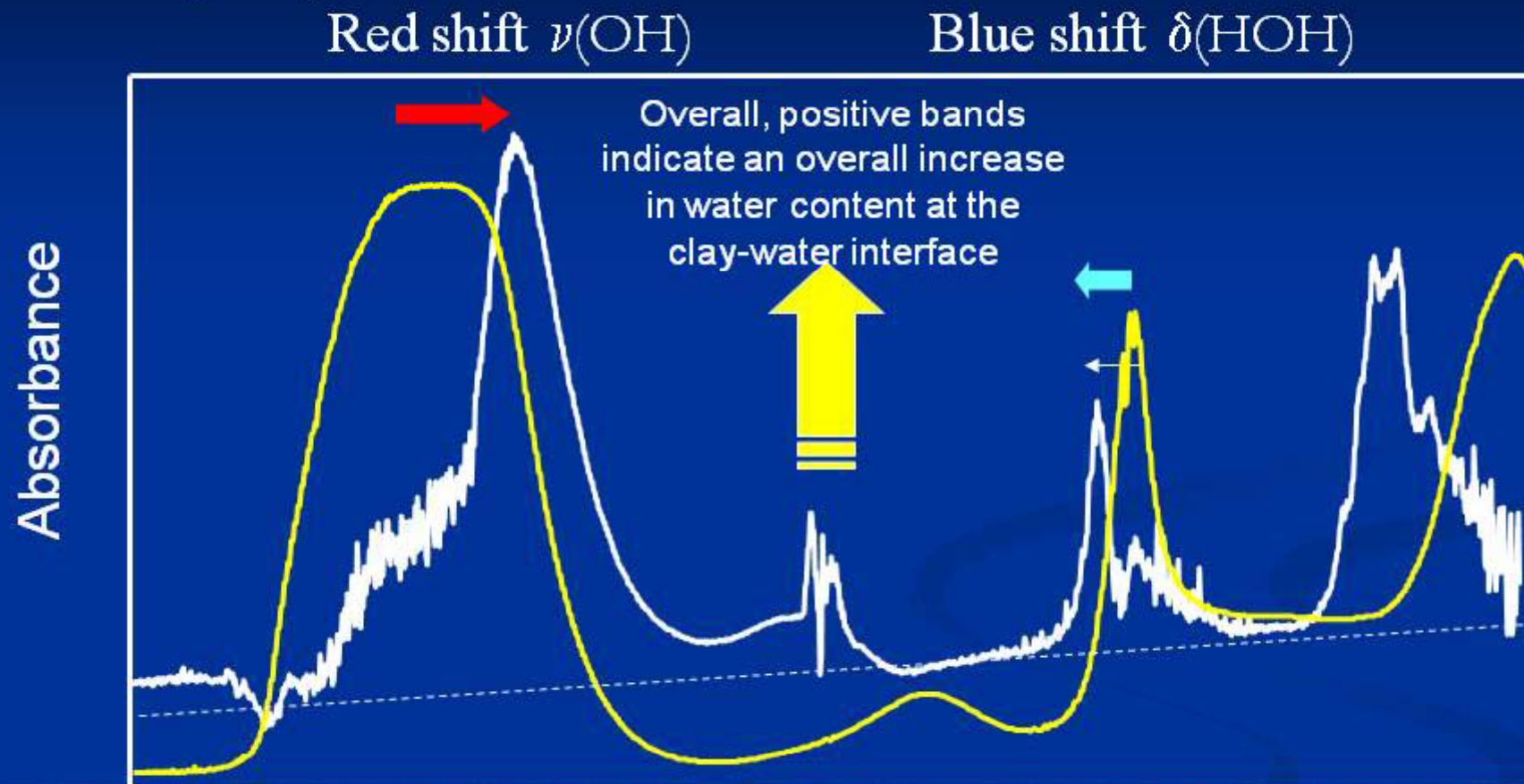
**A:** clay + 0.1 M NaCl





## Mg $\rightarrow$ Na exchange

Comparison: FTIR Mg-SWy<sub>2</sub>-Na-SWy<sub>2</sub> spectrum (white) to the ATR-FTIR spectrum of bulk water (yellow)



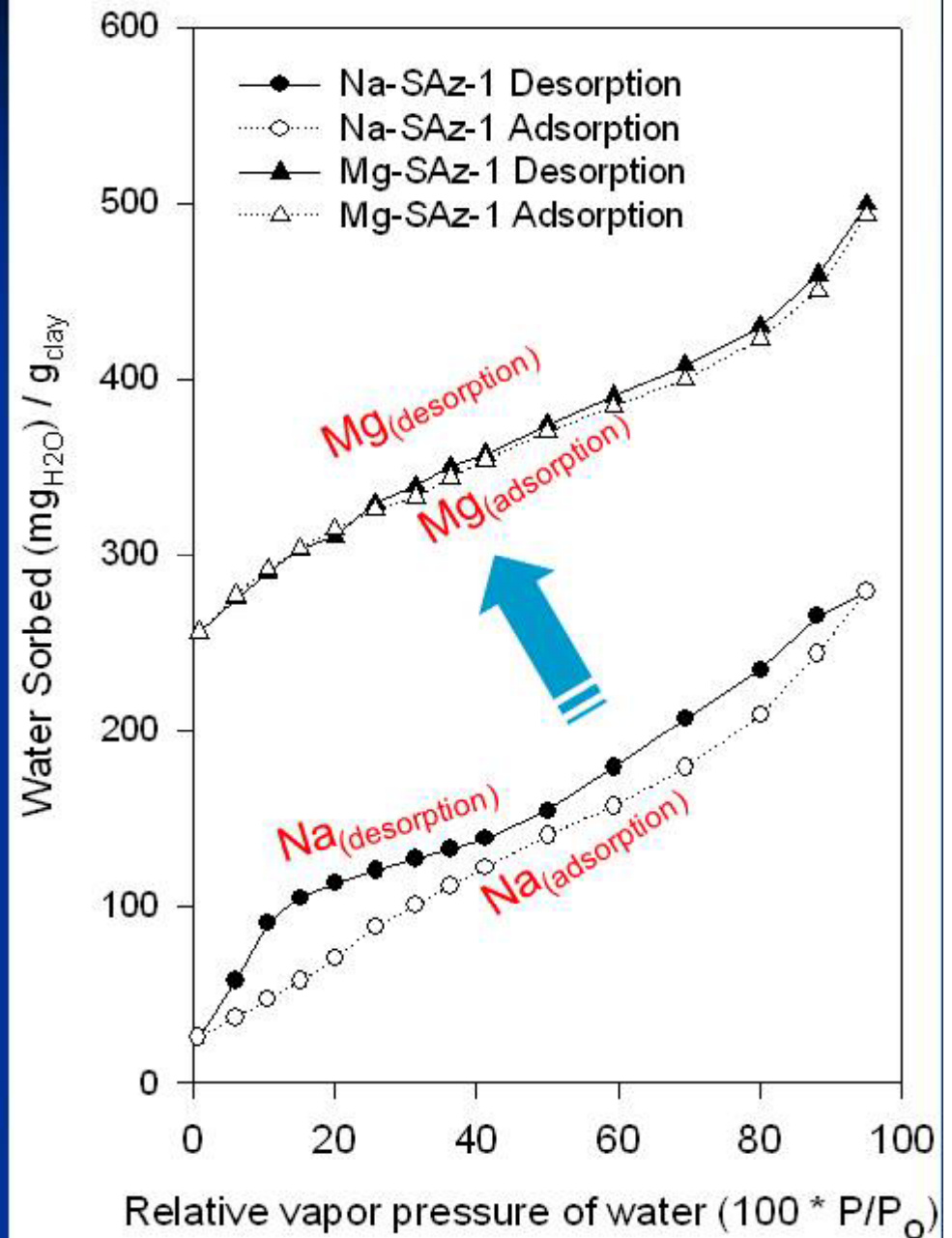
When  $\text{Mg}^{2+}$  exchanges for  $\text{Na}^+$ , the overall water content is increased (as shown by the positive absorbance bands) because the enthalpy of hydration of  $\text{Mg}^{2+}$  is significantly larger than that of  $\text{Na}^+$ . In addition, the 'type' of water sorbed is more strongly hydrogen bonded than bulk water as shown by the red-shift of the  $\nu(\text{OH})$  band, and the blue-shift of the  $\delta(\text{HOH})$  band

# Mg $\rightarrow$ Na exchange

## What happens when $\text{Mg}^{2+}$ replaces $\text{Na}^+$ during cation exchange?

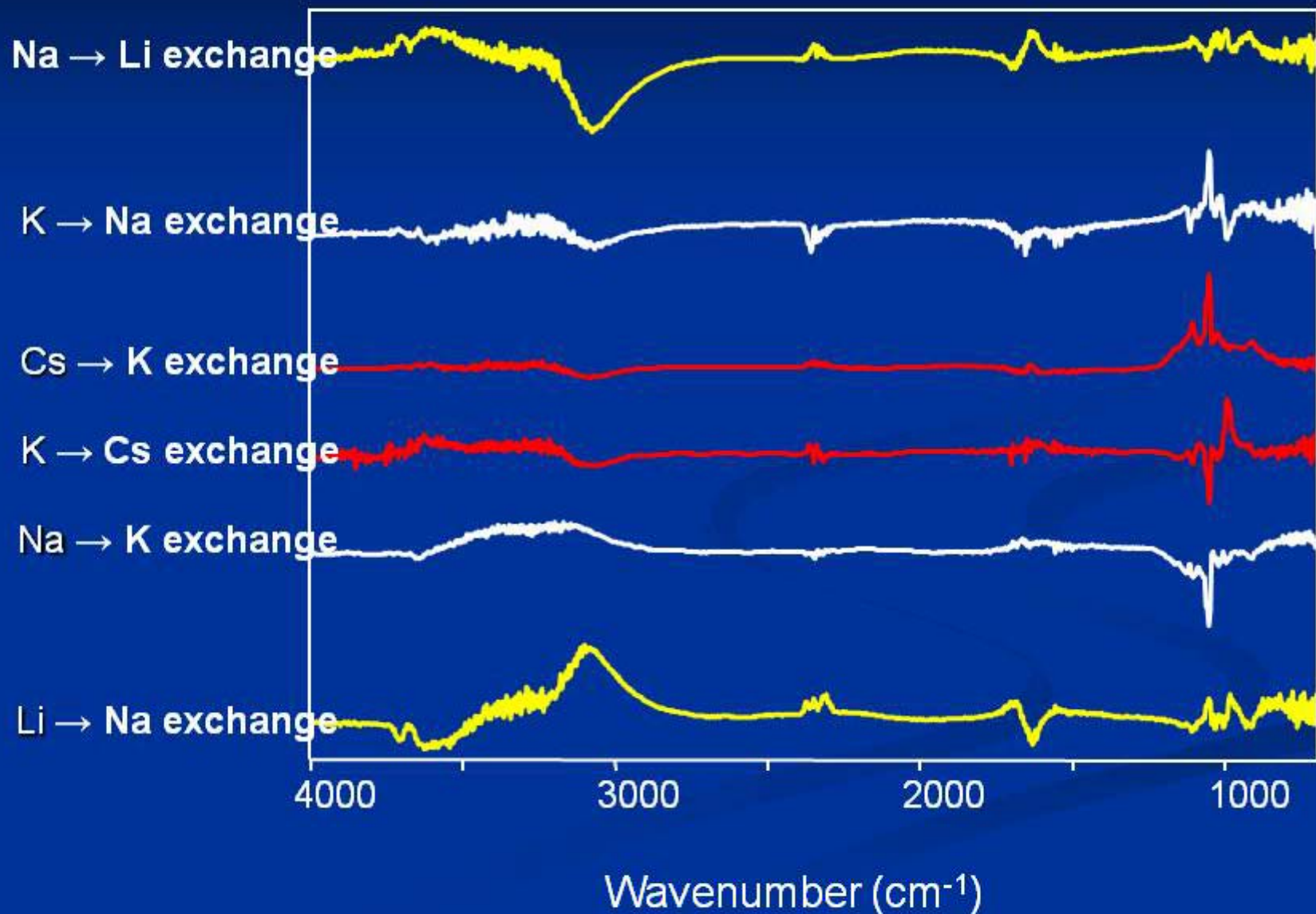
From prior vapor sorption studies of  $\text{H}_2\text{O}$  on Na- and Mg-exchanged SAz-1 smectite we know that the overall water content of the clay is increased.

FTIR spectra provide additional insight about the type of water that is displaced/added during cation exchange

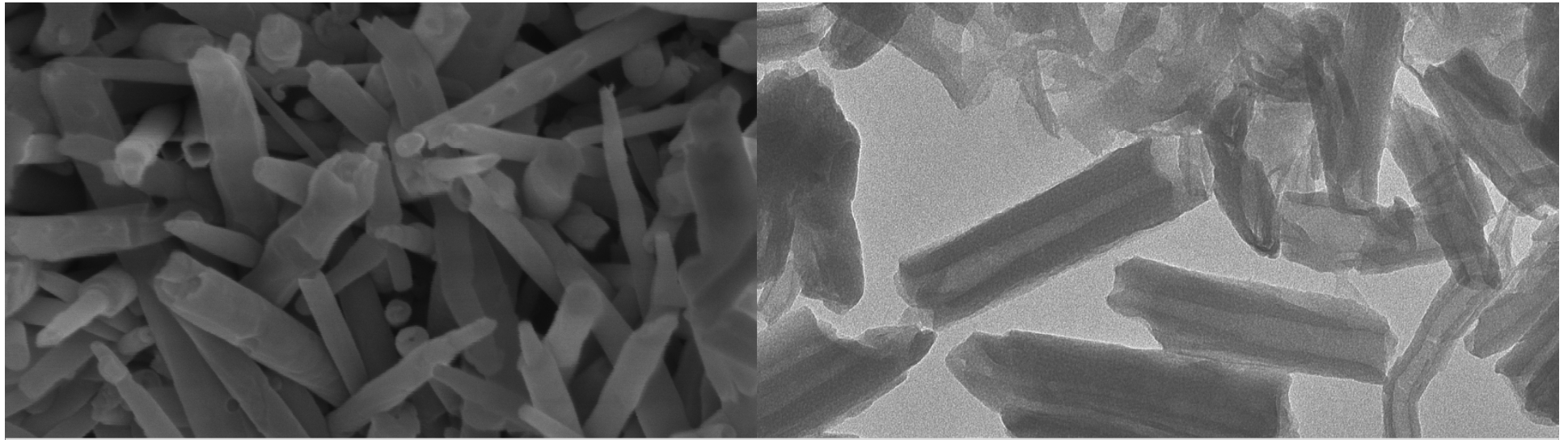




# Cation Exchange of Monovalent Cations

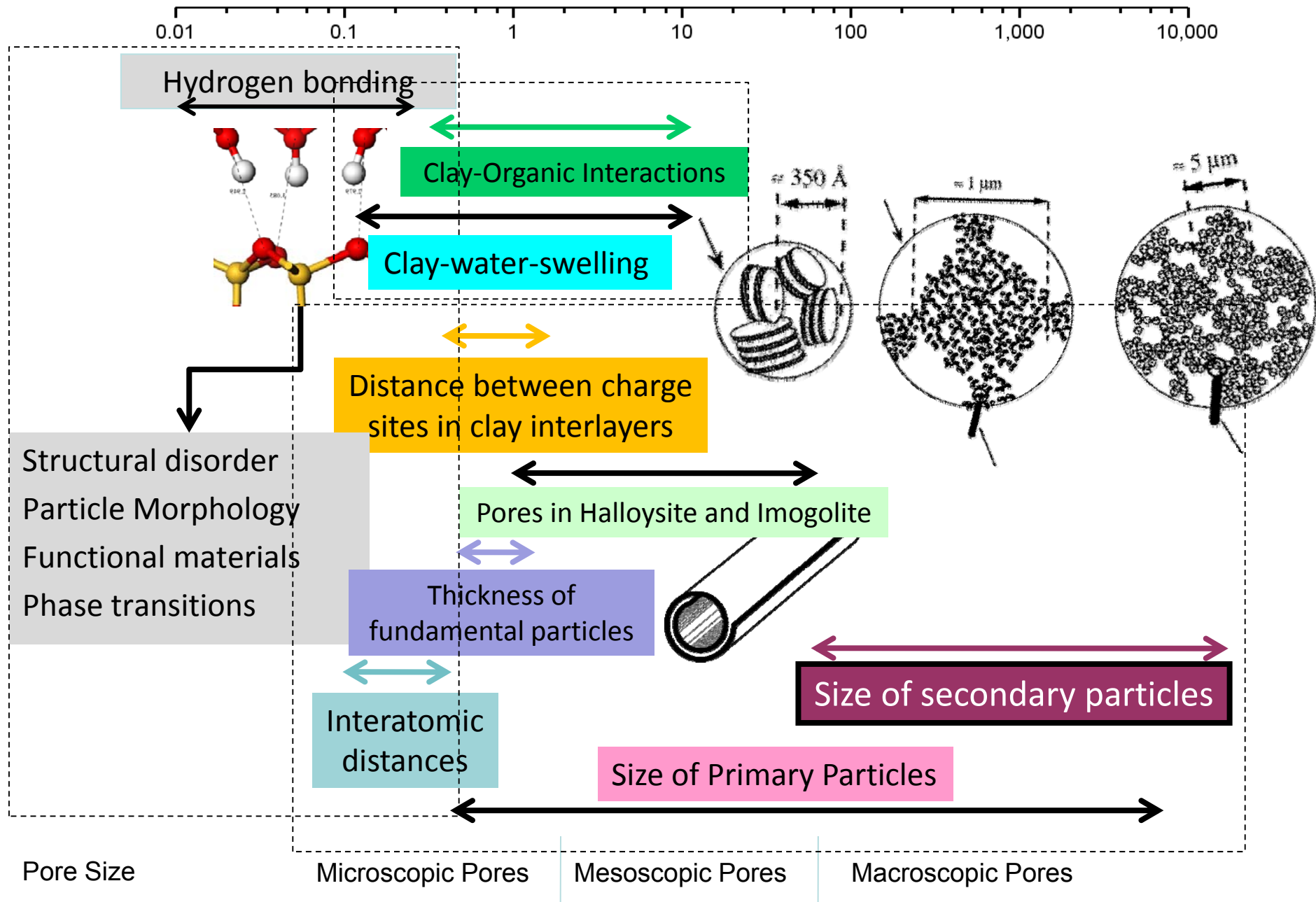






Probing the nanoscale architecture  
of clay minerals and hydrous oxides

(length scale of nanometers)



# Probing the microscopic hydrophobicity of smectite surfaces. A vibrational spectroscopic study of dibenzo-*p*-dioxin sorption to smectite†‡

Kiran Rana,<sup>a</sup> Stephen A. Boyd,<sup>b</sup> Brian J. Teppen,<sup>b</sup> Hui Li,<sup>b</sup> Cun Liu<sup>b</sup>  
and Cliff. T. Johnston<sup>\*a</sup>

*Received 16th December 2008, Accepted 17th February 2009*

*First published as an Advance Article on the web 10th March 2009*

DOI: 10.1039/b822635k



Subscriber access provided by Purdue University Libraries

## Article

### Mechanisms Associated with the High Adsorption of Dibenzo-*p*-dioxin from Water by Smectite Clays

Cun Liu, Hui Li, Brian J. Teppen, Cliff T. Johnston, and Stephen A. Boyd

*Environ. Sci. Technol.*, Article ASAP • DOI: 10.1021/es802381z • Publication Date (Web): 20 March 2009

Downloaded from <http://pubs.acs.org> on April 8, 2009



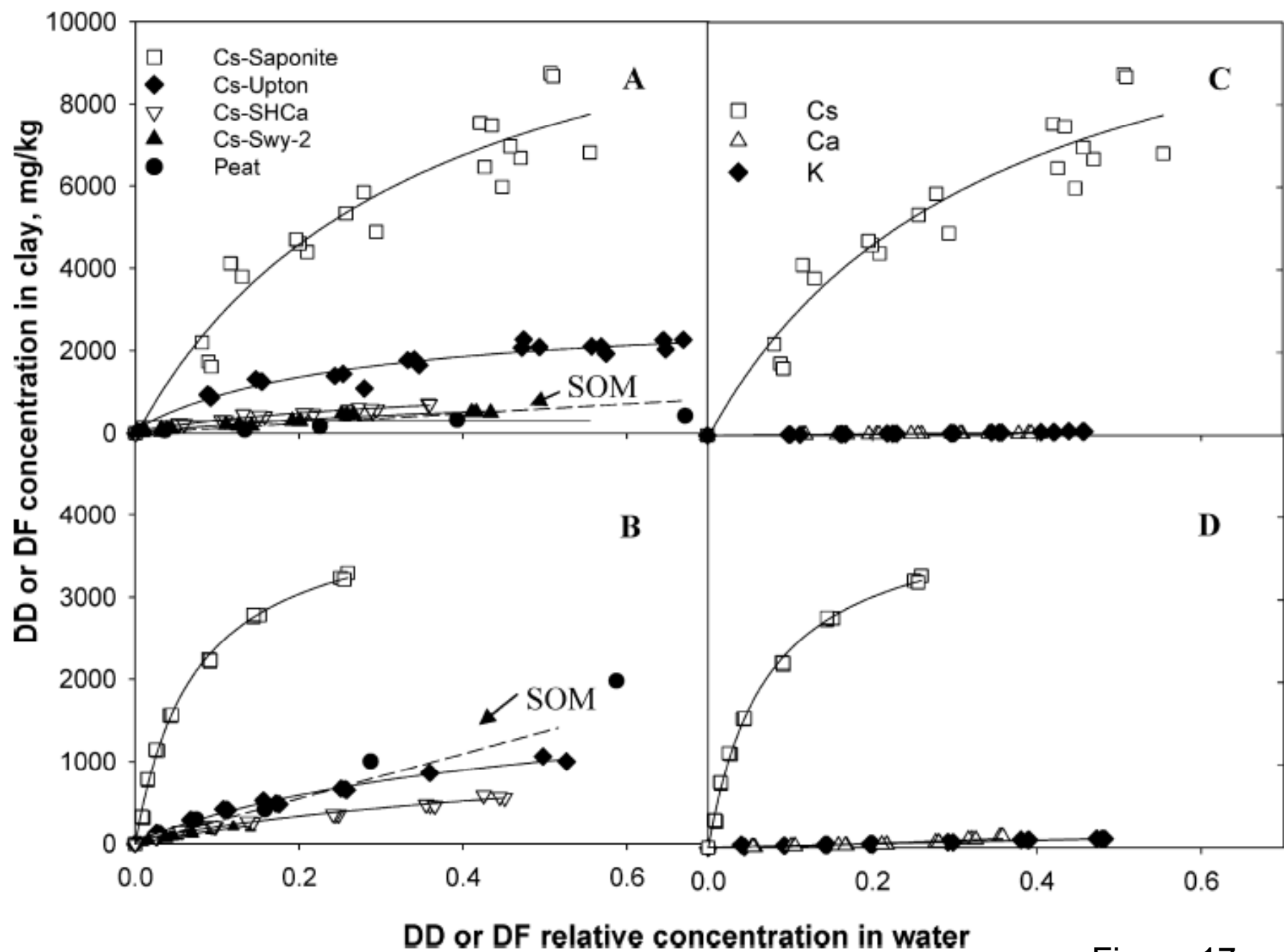


Figure 17

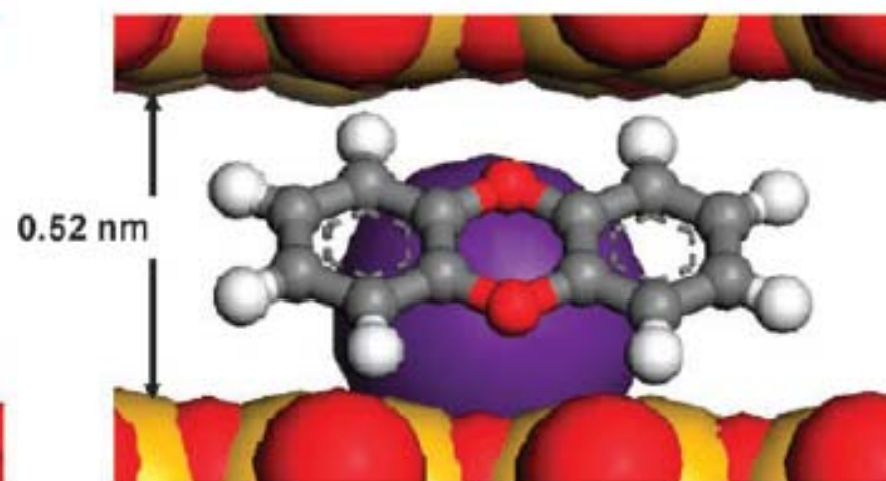
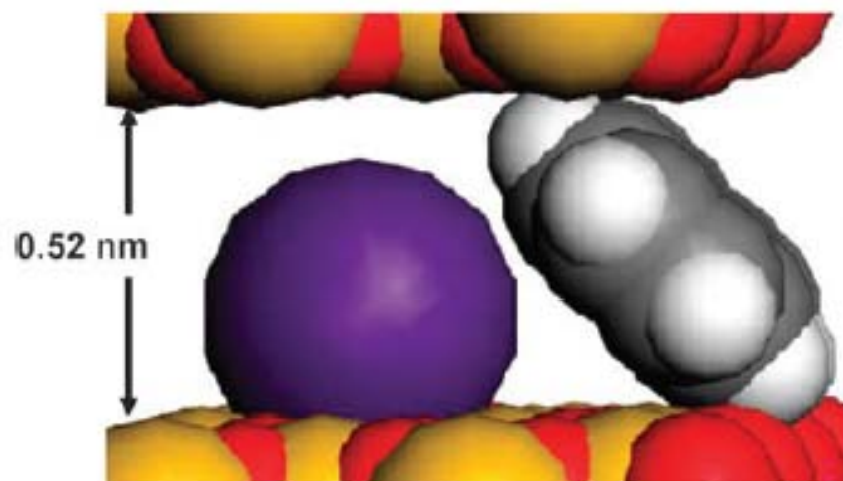
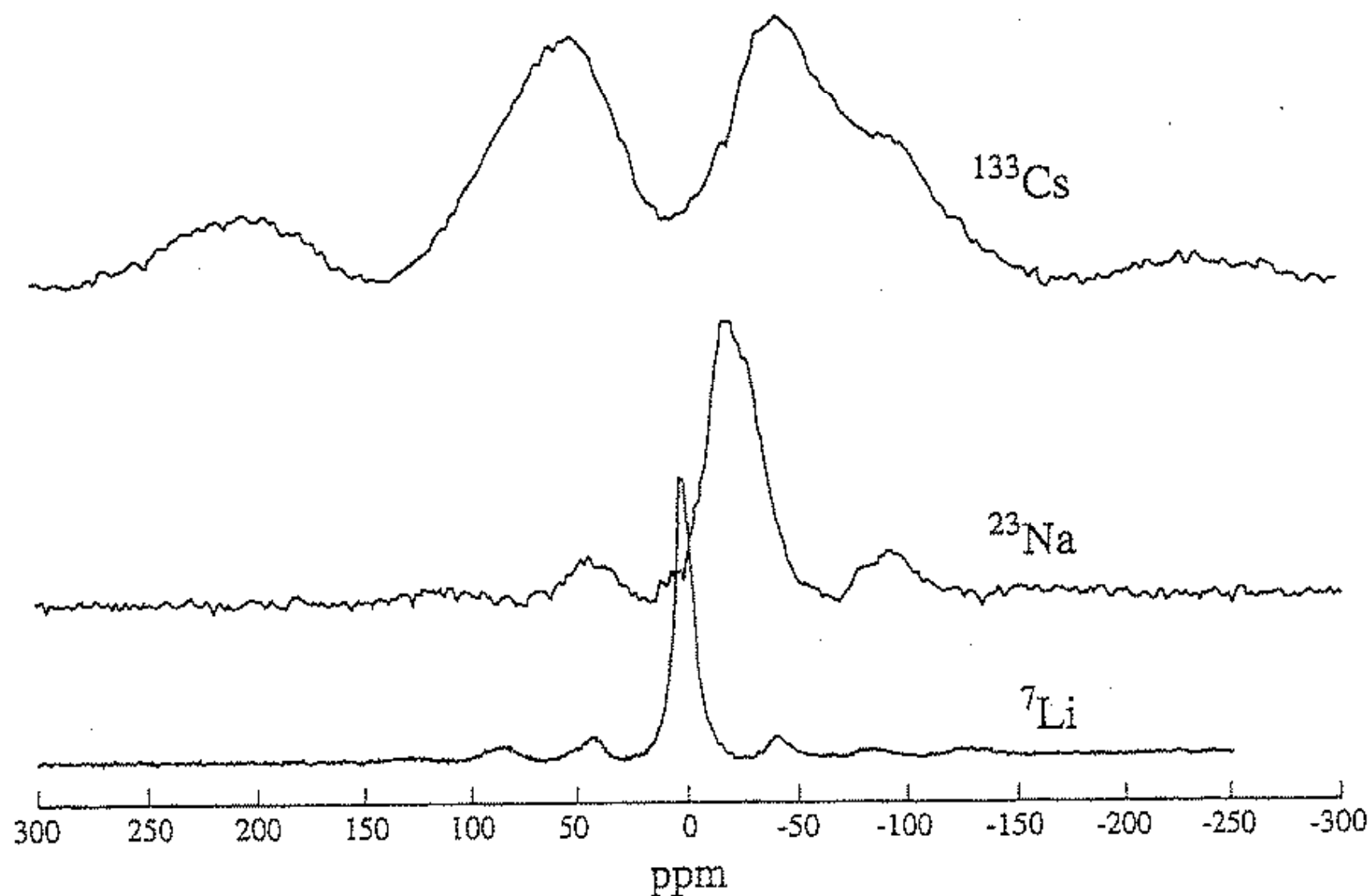


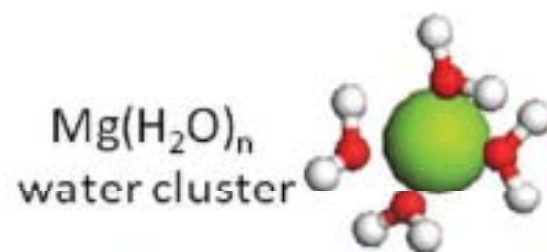
Figure 18



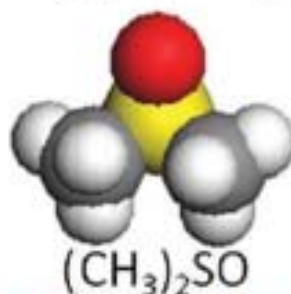
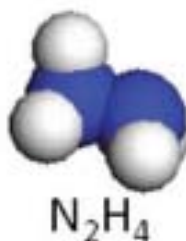
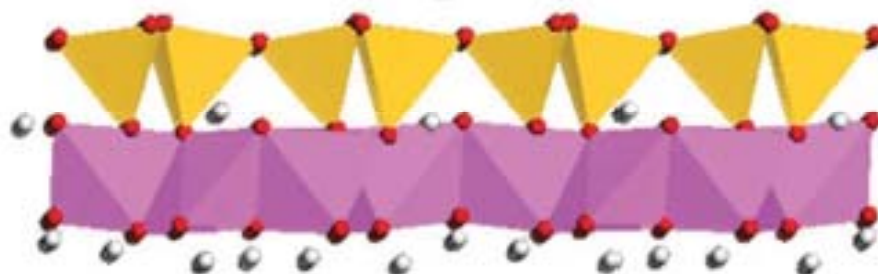
**Figure 10.7** The  $^{23}\text{Na}$ ,  $^{133}\text{Cs}$ , and  $^7\text{Li}$  spectra of SAz-1 which was substituted with the cations. The zero for the chemical shift scale for all three spectra is set at the position of the resonance of 1 M aqueous solutions of LiCl, NaCl, and CsCl.



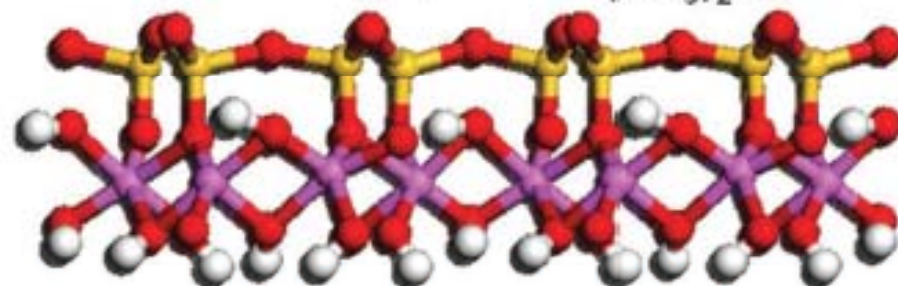
Exchangeable cations:  
 ${}^6\text{Li}$ ,  ${}^{23}\text{Na}$ ,  ${}^{39}\text{K}$ ,  ${}^{113}\text{Cd}$ ,  ${}^{133}\text{Cs}$



Interfacial water:  
 ${}^{17}\text{O}$ ,  ${}^1\text{H}$ ,  ${}^2\text{H}$



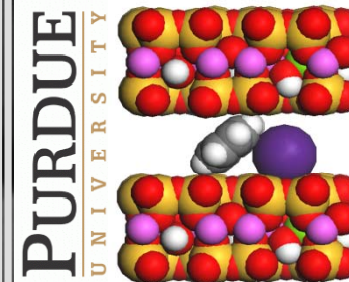
Water and organic solutes:  
 ${}^{13}\text{C}$ ,  ${}^{15}\text{N}$ ,  ${}^{31}\text{P}$ ,  ${}^{17}\text{O}$ ,  ${}^{19}\text{F}$ ,  ${}^1\text{H}$ ,  ${}^2\text{H}$



Structural nuclei:  
 ${}^{29}\text{Si}$ ,  ${}^{27}\text{Al}$ ,  ${}^{17}\text{O}$ ,  ${}^{19}\text{F}$ ,  ${}^1\text{H}$ ,  ${}^2\text{H}$

FIG. 12. A conceptual picture of the NMR-active nuclei used to study clay minerals, clay-water, cation exchange, and clay-organic interactions.

# Acknowledgements



- Prof. Masaru Mizoguchi for the invitation to come to Japan.
- Collaborators:
  - Steve Boyd, Brian Teppen, Hui Li
- Students and postdocs
  - Bushra Khan, Kiran Rana, Kamol Dad
- Funding sources: NSF, EPA, NIH and USDA