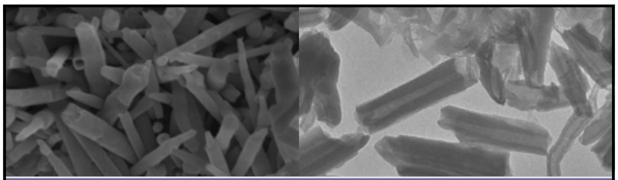


Role of clay minerals in controlling the fate and transport of radioactive ^{137,134}Cs in soils

30 May 2011
University of Tokyo
Cliff T. Johnston[1] & Stephen F. Agnew[2]
[1]*Purdue University, West Lafayette, IN*
[2]*Columbia Energy & Environmental Services*

PURDUE UNIVERSITY

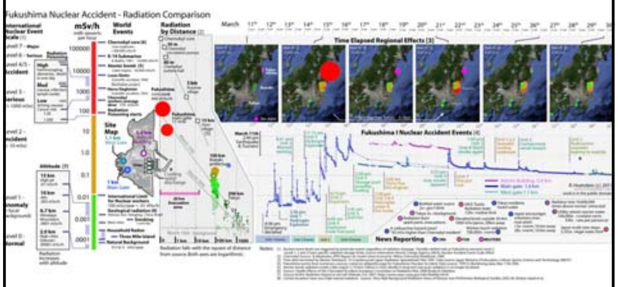
Columbia Energy AND ENVIRONMENTAL SERVICES

Overview

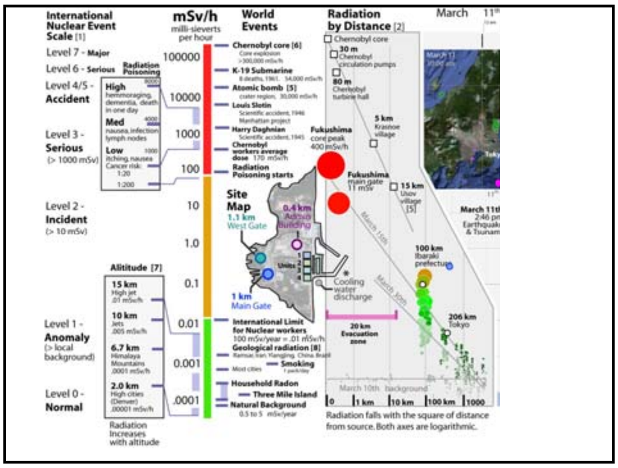
- Fukushima accident
- Movement of ^{137}Cs in soils
- Behavior of ^{137}Cs in soils
- Molecular Interactions of Cs with clay minerals

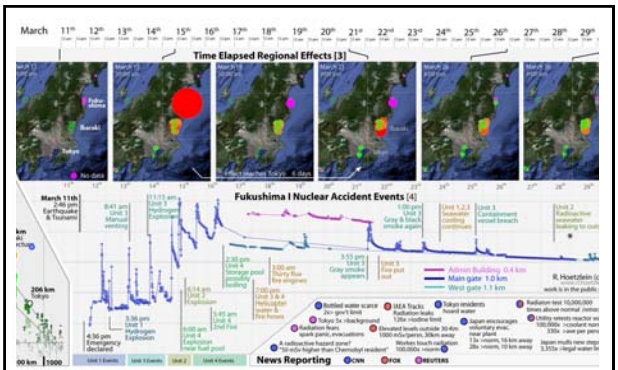
Fukushima Accident

- 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.



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





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

Sampling spot	【fixed point①】*1 Playground (west-northwest approx. 500m)*2		【fixed point②】*1 Forest of wild birds (west approx. 500m)*2		【fixed point③】*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
I-131(approx. 8 days)	9.4E+04	9.4E+04	2.0E+04	9.9E+03	9.1E+04	1.1E+05
I-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+06	1.4E+06
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cs-137(approx. 30 years)	5.0E+05	5.2E+05	4.0E+04	1.5E+04	1.1E+06	1.4E+06
Te-129m(approx. 34 days)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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^3 in 2002, which is 180 Bq/kg dry soil at 1700 kg/m^3.
- http://www.energy.gov/news/documents/040711__AMS_Data_April_7__v3.pptx

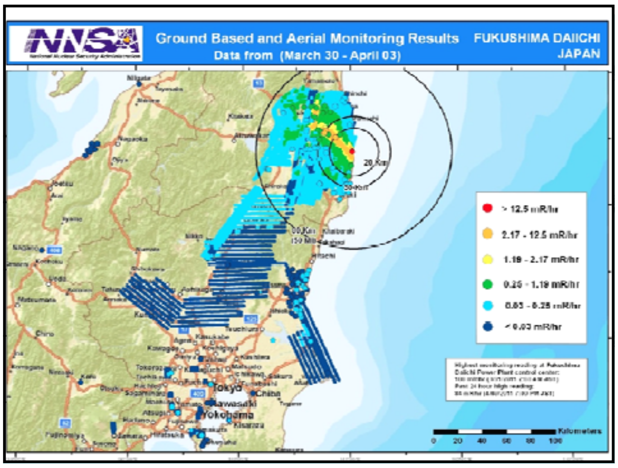
Radiation Maps

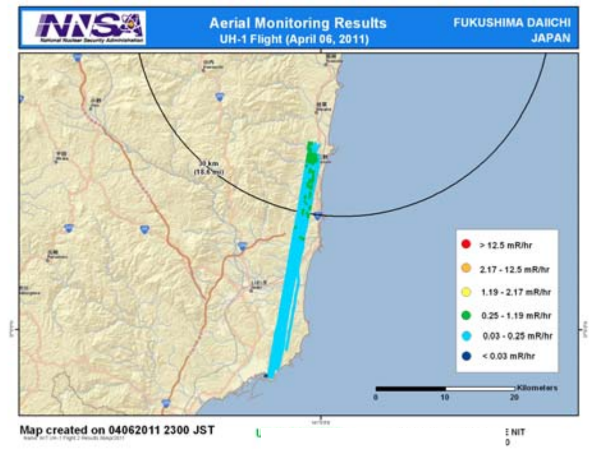
- Result of an aerial survey by DOE NNSA with their special plane.
- Collaboration with Japan's Nuclear and Industrial Safety Agency (NISA)
- Some contamination extends beyond the 30 km limit.

- 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





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

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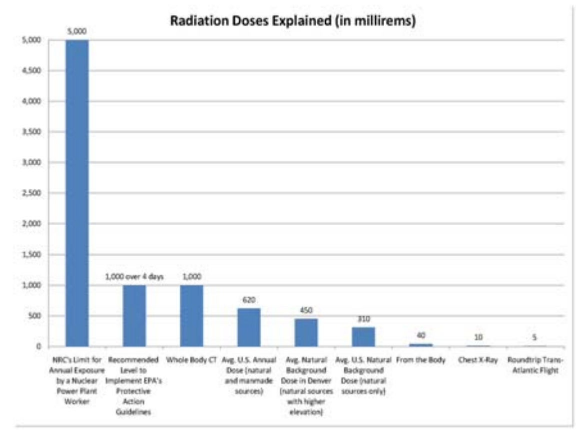
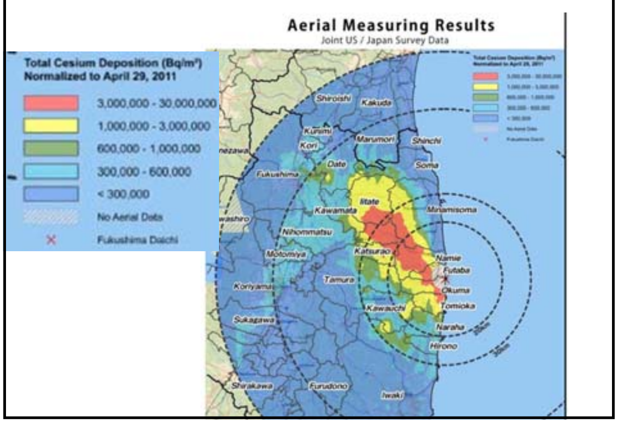
Context

- 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

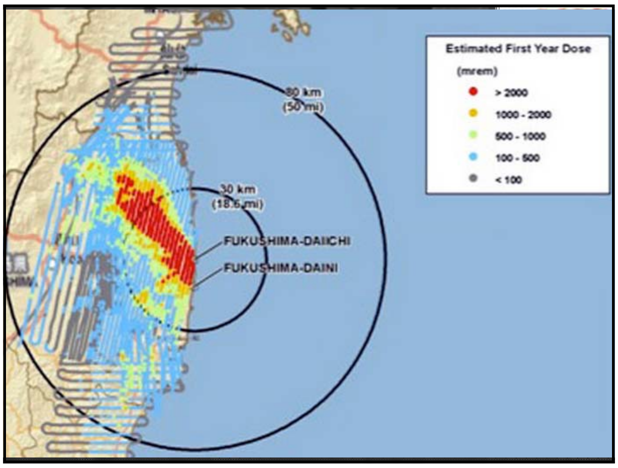


http://www.iaea.org/newscenter/news/tsunamiupdate01.html



Projected dose map

- 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

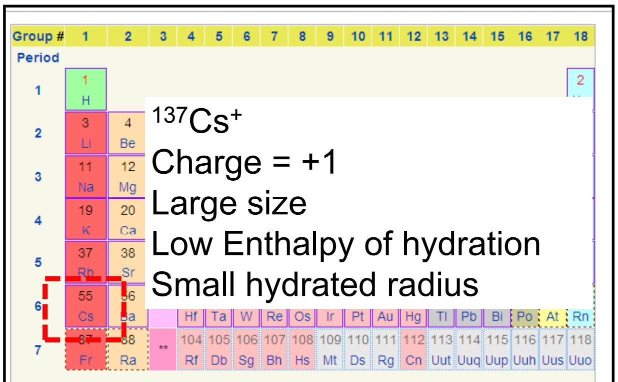


Fukushima contamination comparison

- 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}Cs in Soils: The Role of Clay Minerals

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



Movement of 137-Cs in soils

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

J. Environ. Qual. 22:722–730 (1993).

Vertical migrations of ^{137}Cs

- Slow vertical movement of 137-Cs in soils and sediments
- Next figure – compare 137-Cs to 99-Tc or 3-H

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

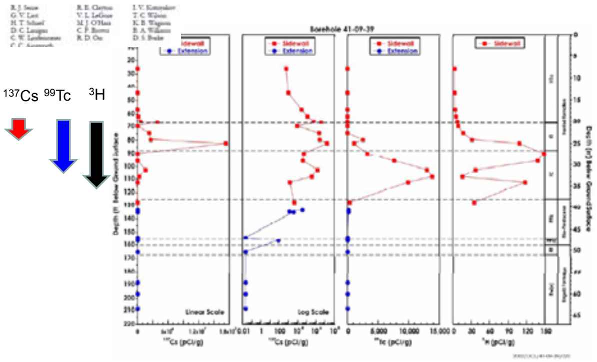


Figure 5.3. Cesium-137, Technetium-99, Strontium-90, and Tritium in Sediments from Table 5.11 Versus Depth with Geology Breaks

General Behavior of ^{137}Cs in soils

- High selectivity
- Sorption models
- Kinetics

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

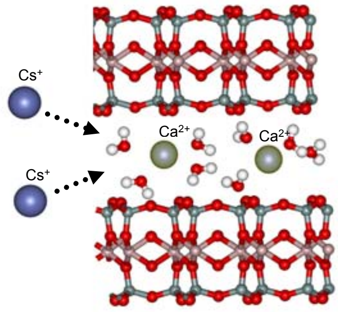
Research has shown that a small fraction of the 'active sites' on clay mineral have a very high affinity for ^{137}Cs

Ion Exchange

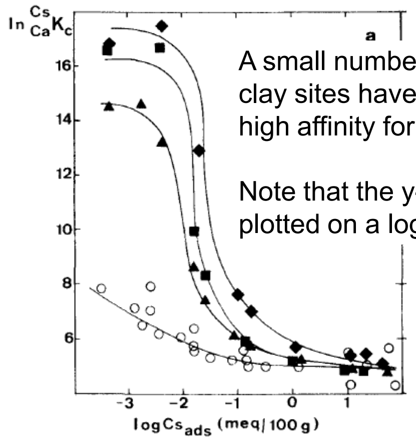
- Ion Exchange
- $2\,Cs^{+} + CaX_2 = 2CsX + Ca^{2+}$

$$K_c = \frac{\{CsX\}^2 (Ca^{2+})}{\{CaX_2\}(Cs^{+})^2}$$

Cation exchange of Ca^{2+} by 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 Cs^+.
- However, these sites are very limited.
- The highest energy sites have a Ln K_c of 33.8 ($\Delta G_{exchange}$ = 40 kJ/mol)
- But represent only a very trace fraction of the total sites:
  - 0.0002% of total sites!

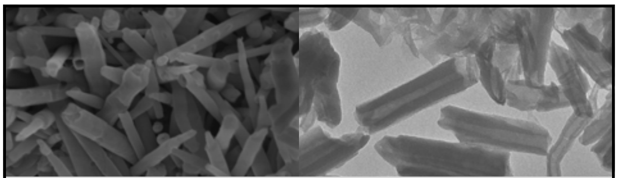
FREUNDLICH AND DUAL LANGMUIR ISOTHERM MODELS FOR PREDICTING ^{137}Cs BINDING ON SAVANNAH RIVER SITE SOILS

Momoko Goto,* Robert Rosson,[†] J. Marion Wampler,[‡] W. Crawford Elliott,[§] Steven Serkiz,** and Bernd Kahn[†]

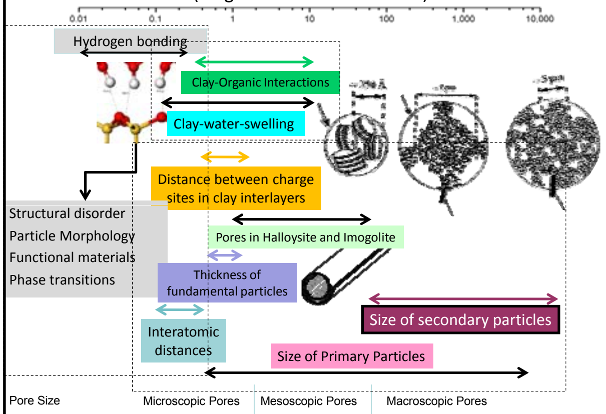
Health Physics January 2008, Volume 94, Number 1

Soil sample	Added cesium[a] (μeq)	^{137}Cs In solution (kBq L^{-1})	^{137}Cs On soil[b] (kBq kg^{-1})	K_d^c (L kg^{-1})
Fuquay	1.24×10^{-3}	0.250	352	1,410 ± 60
	3.75×10^{-1}	0.810	330	410 ± 10
	1.78×10^{0}	1.05	314	300 ± 10
Orangeburg	1.24×10^{-3}	0.136	350	2,570 ± 100
		0.169	340	2,010 ± 90
	3.75×10^{-1}	1.17	311	270 ± 10
		1.02	311	300 ± 10
				157 ± 7
				166 ± 7
				1,100 ± 50
				149 ± 6
				137 ± 6
Blanton	1.24×10^{-3}	0.533	332	620 ± 20
	7.25×10^{-2}	2.82	248	88 ± 4
	3.75×10^{-1}	3.51	220	63 ± 3
Vaucluse	1.24×10^{-3}	0.831	325	390 ± 20
		1.09	314	290 ± 10
	7.25×10^{-2}	2.73	250	92 ± 4
		2.83	250	89 ± 4
	3.75×10^{-1}	4.02	199	50 ± 3
		4.01	197	49 ± 3

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



Introduction to the nanoscale architecture of clay minerals



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

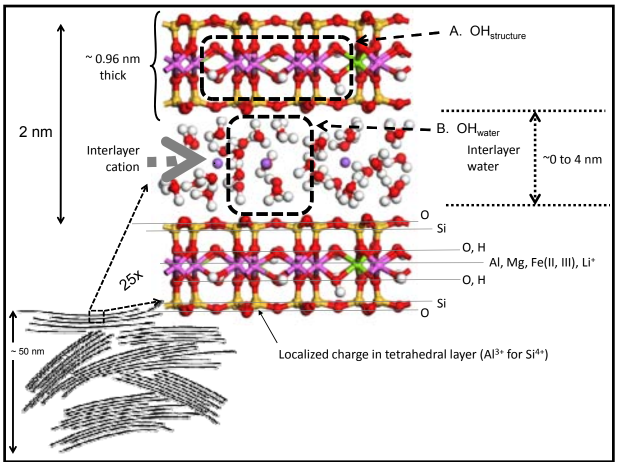
J. P. McKinley et al.,Environ.*Sci.Technol.* *35 (17):3433-3441, 2001.*

- The retention of $^{137}Cs^{+}$ by sediments and phyllosilicates has been intensively studied since anthropogenic $^{137}Cs^{+}$ 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).

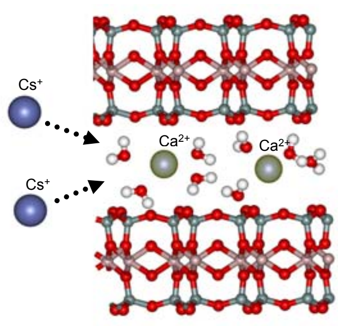
Proposed model. Three different chemical surface sites:

- 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}Cs from FES.

Nonselective exchange sites

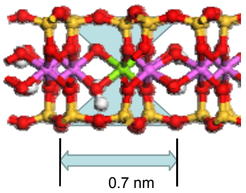


Cation exchange of Ca^{2+} by Cs^{+}



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

Isomorphous Substitution of Mg → Al in the octahedral layer (montmorillonite)



Isomorphous Substitution of Al → Si in the tetrahedral layer (saponite)

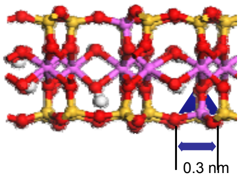
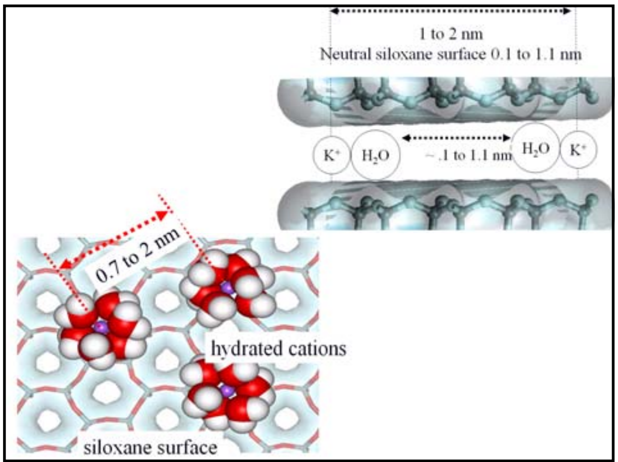
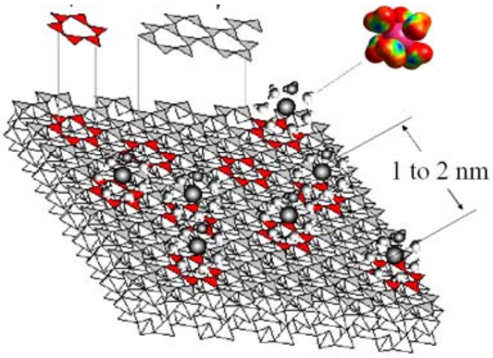
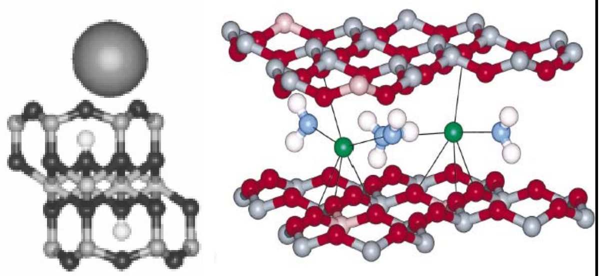


Figure 8



Hydrophilic Sites (red) Hydrophobic sites (grey)





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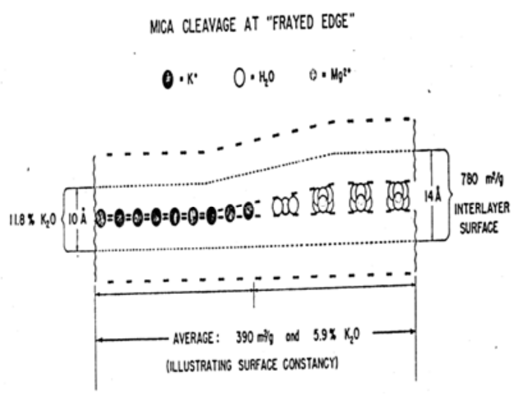
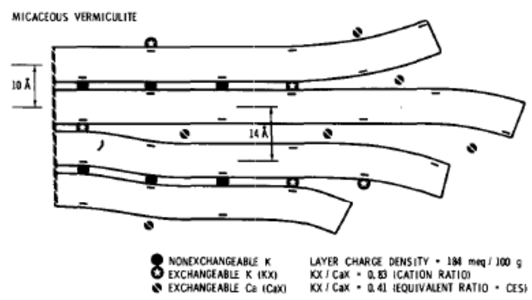
Selective frayed edge sites (FES) on micas





Cation Exchange Selectivity of Some Clay-Sized Minerals and Soil Materials[1]

D. L. Dolcater, E. G. Lotse, J. K. Syers, and M. L. Jackson[2] Soil Sci. Soc. Amer. Proc., Vol. 32, 1968

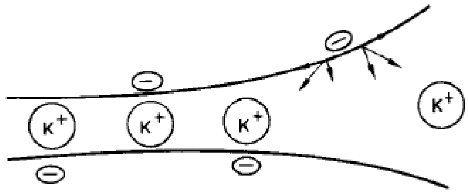


Fig. 1. Selective sorption of a K^+ ion in a frayed edge of a weathered mica sheet.

Sorption behavior linked to specific exchange sites:

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

Kinetics of Cs exchange

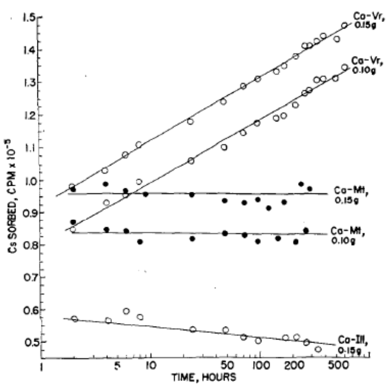


Fig. 1—Sorption of Cs by Ca-saturated clay minerals with time. Ill = illite, Mt = montmorillonite, Vr = vermiculite.

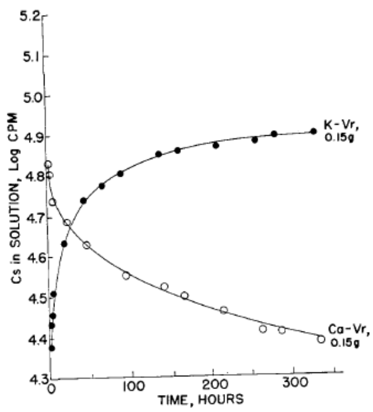
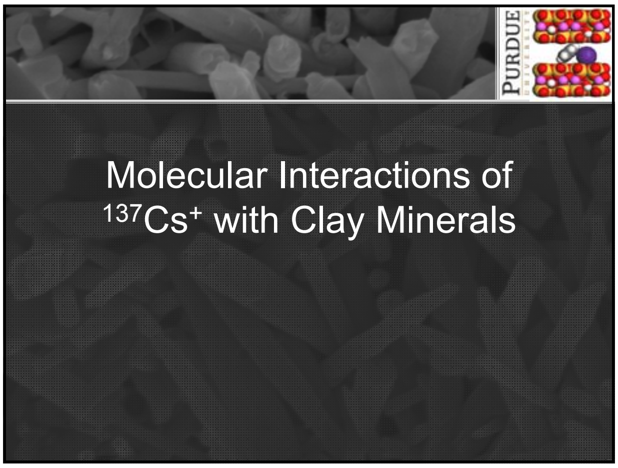
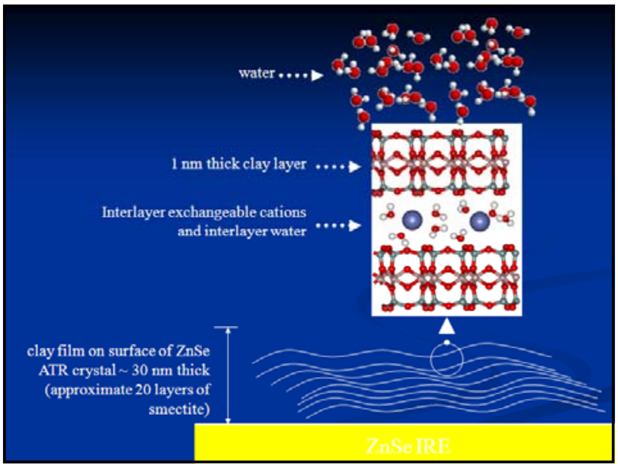
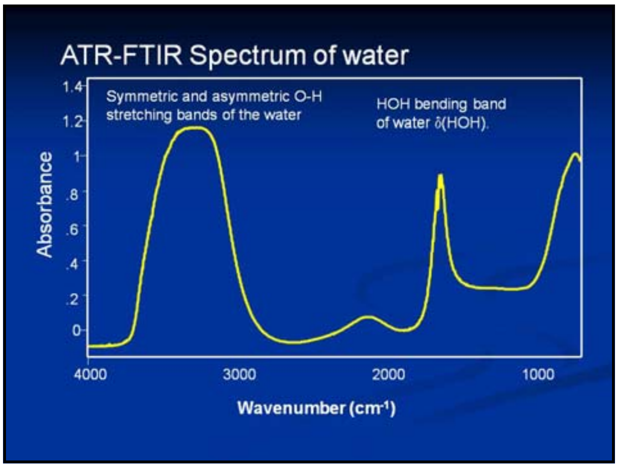
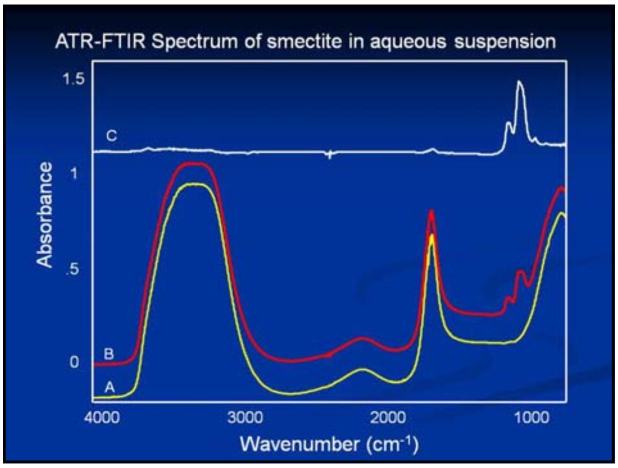


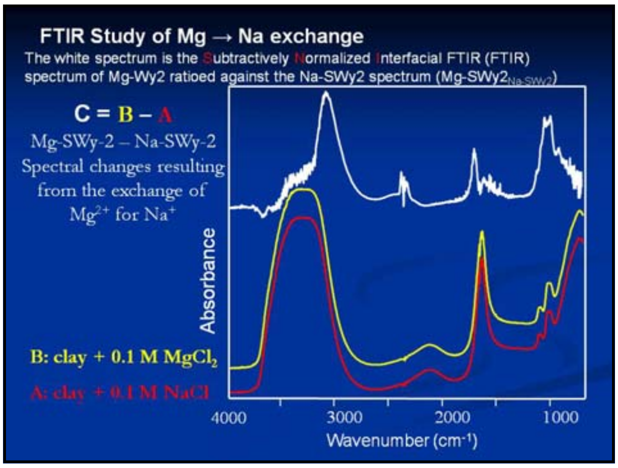
Fig. 5—Diffusion of Cs into Ca-saturated vermiculite and its release from K-saturated vermiculite.

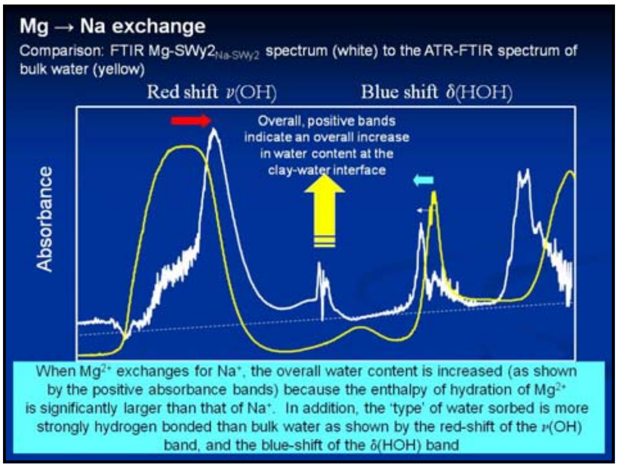

PURDUE
Molecular Interactions of
$^{137}Cs^{+}$ with Clay Minerals

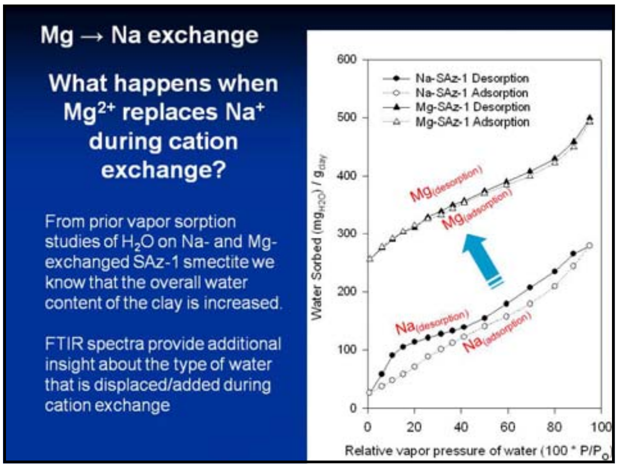

water
1 nm thick clay layer
Interlayer exchangeable cations
and interlayer water
clay film on surface of ZnSe
ATR crystal ~ 30 nm thick
(approximate 20 layers of
smectite)
ZnSe IRE

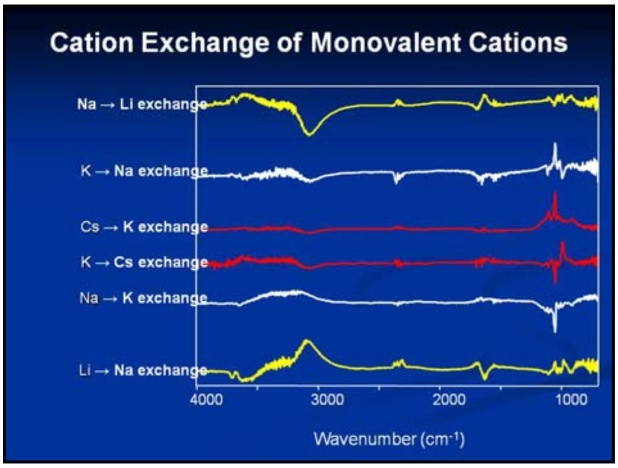

ATR-FTIR Spectrum of water
Symmetric and asymmetric O-H
stretching bands of the water
HOH bending band
of water δ(HOH).
Absorbance
Wavenumber (cm^{-1})

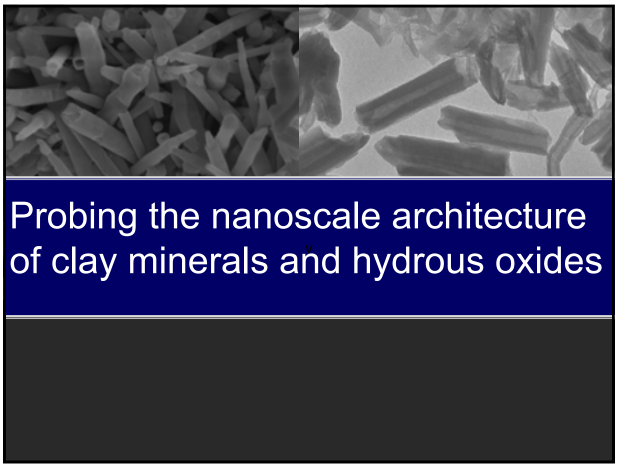

ATR-FTIR Spectrum of smectite in aqueous suspension
C
B
A
Absorbance
Wavenumber (cm^{-1})

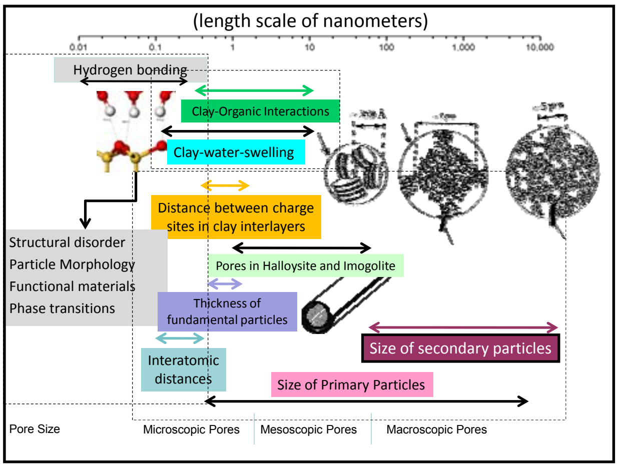

FTIR Study of Mg → Na exchange
The white spectrum is the Subtractively Normalized Interfacial FTIR (FTIR)
spectrum of Mg-Wy2 ratioed against the Na-SWy2 spectrum (Mg-SWy2$_{Na\text{-}SWy2}$)
C = B – A
Mg-SWy-2 – Na-SWy-2
Spectral changes resulting
from the exchange of
Mg^{2+} for Na^{+}
Absorbance
B: clay + 0.1 M $MgCl_2$
A: clay + 0.1 M NaCl
Wavenumber (cm^{-1})

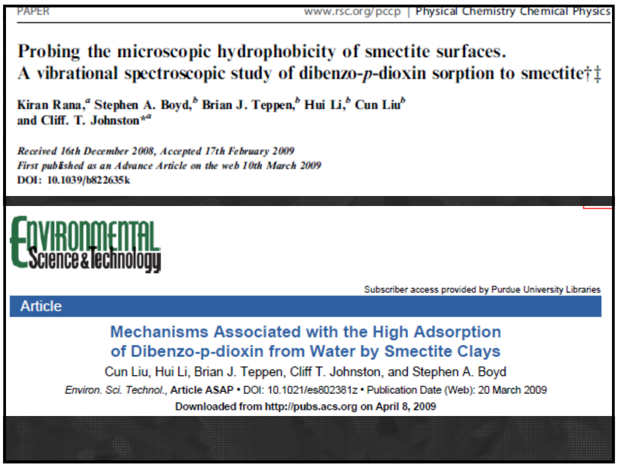

Mg → Na exchange
Comparison: FTIR Mg-SWy2$_{Na\text{-}SWy2}$ spectrum (white) to the ATR-FTIR spectrum of
bulk water (yellow)
Red shift ν(OH)
Blue shift δ(HOH)
Overall, positive bands
indicate an overall increase
in water content at the
clay-water interface
Absorbance
When Mg^{2+} exchanges for Na^{+}, the overall water content is increased (as shown
by the positive absorbance bands) because the enthalpy of hydration of Mg^{2+}
is significantly larger than that of Na^{+}. In addition, the 'type' of water sorbed is more
strongly hydrogen bonded than bulk water as shown by the red-shift of the ν(OH)
band, and the blue-shift of the δ(HOH) band


Mg → Na exchange
What happens when Mg²⁺ replaces Na⁺ during cation exchange?
From prior vapor sorption studies of H₂O 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
Na-SAz-1 Desorption
Na-SAz-1 Adsorption
Mg-SAz-1 Desorption
Mg-SAz-1 Adsorption
Mg(desorption)
Mg(adsorption)
Na(desorption)
Na(adsorption)
Water Sorbed (mg_H2O) / g_clay
Relative vapor pressure of water (100 * P/P₀)


Cation Exchange of Monovalent Cations
Na → Li exchange
K → Na exchange
Cs → K exchange
K → Cs exchange
Na → K exchange
Li → Na exchange
4000
3000
2000
1000
Wavenumber (cm⁻¹)


Probing the nanoscale architecture of clay minerals and hydrous oxides


(length scale of nanometers)
Hydrogen bonding
Clay-Organic Interactions
Clay-water-swelling
Distance between charge sites in clay interlayers
Structural disorder
Particle Morphology
Functional materials
Phase transitions
Pores in Halloysite and Imogolite
Thickness of fundamental particles
Size of secondary particles
Interatomic distances
Size of Primary Particles
Pore Size
Microscopic Pores
Mesoscopic Pores
Macroscopic Pores


PAPER
www.rsc.org/pccp | Physical Chemistry Chemical Physics
Probing the microscopic hydrophobicity of smectite surfaces.
A vibrational spectroscopic study of dibenzo-p-dioxin sorption to smectite†‡
Kiran Rana,a Stephen A. Boyd,b Brian J. Teppen,b Hui Li,b Cun Liub and Cliff. T. Johnston*a
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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
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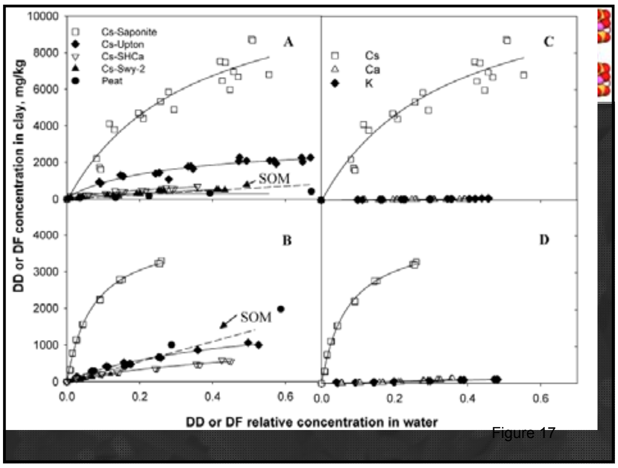
Cs-Saponite
Cs-Upton
Cs-SHCa
Cs-Swy-2
Peat
A
B
C
D
Cs
Ca
K
SOM
DD or DF concentration in clay, mg/kg
DD or DF relative concentration in water
Figure 17

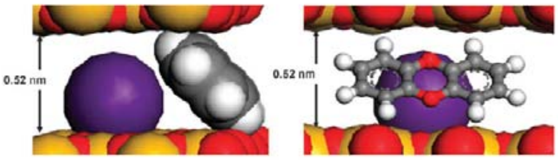

Figure 18

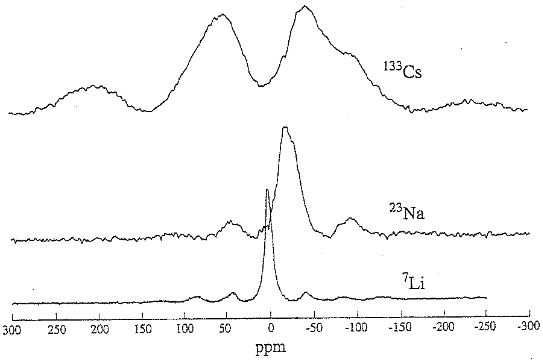

Figure 10.7 The ^{23}Na, ^{133}Cs, and ^{7}Li spectra of SAz-1 which was substituted with the cations. The zero for the chemical shift scale for all three spectra is set at the position of the resonance of 1 M aqueous solutions of LiCl, NaCl, and CsCl.

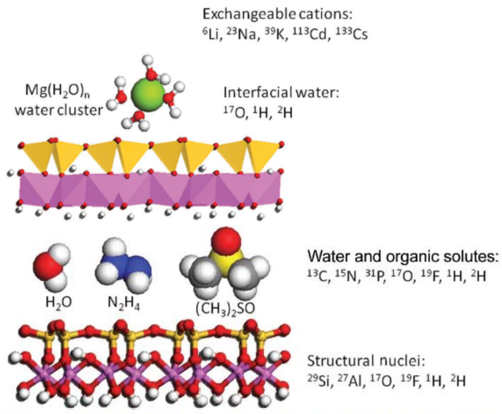

FIG. 12. A conceptual picture of the NMR-active nuclei used to study clay minerals, clay-water, cation exchange, and clay-organic interactions.

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