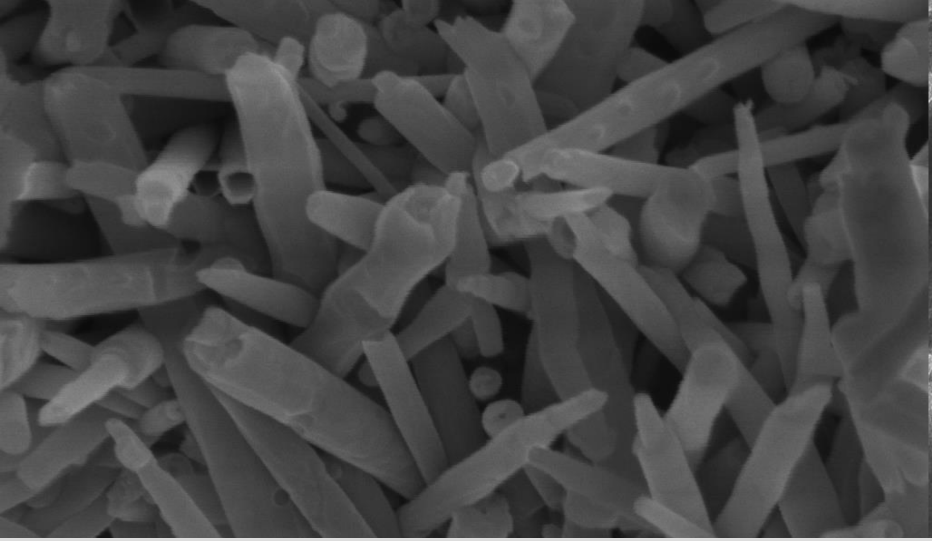

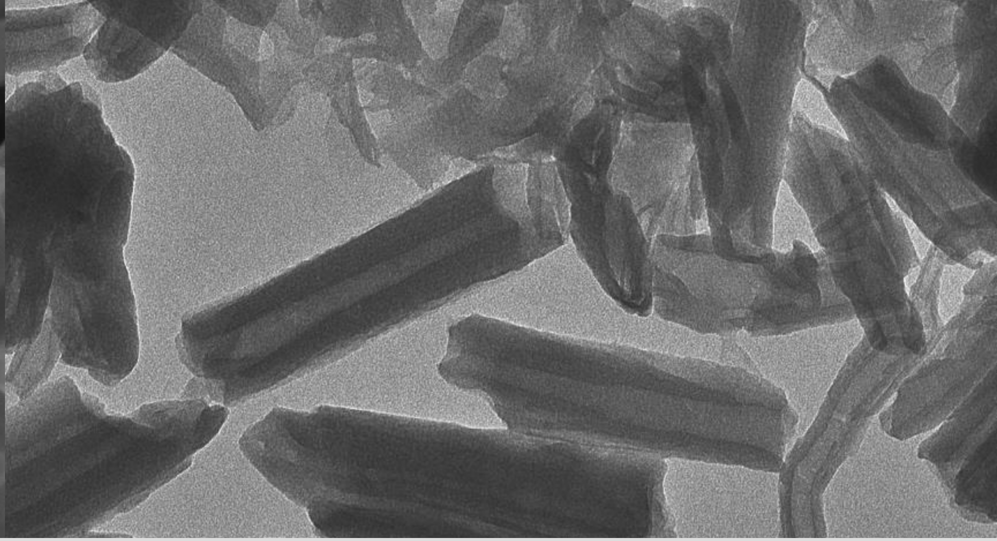

Role of clay minerals in controlling the fate and transport of radioactive Cs in soils

Battles of Soil Scientists
in Fukushima, Japan

4 November 2013

Cliff T. Johnston
Purdue University, West Lafayette, IN

PURDUE UNIVERSITY

特別セミナー

粘土表面の放射性セシウムの吸着特性とその挙動

The sorption and transport behaviors of radioactive Cs ion on clay minerals

Cs

2011年5月30日（月）
15:00-16:30

東京大学大学院農学生命科学研究科
フードサイエンス棟 中島董一郎記念ホール
（東京都文京区弥生1-1-1）http://www.a.u-tokyo.ac.jp/nakashima/

参加無料：
事前申込不要
講演言語：
英語（通訳なし）

趣旨：東日本大震災に伴う福島原発事故では放射性セシウムで汚染された土壌の修復が急務の解決課題です。この課題を考える上で重要なのは、2μm 以下と定義される粘土粒子とセシウムの吸着・脱着特性、およびセシウムを吸着した粘土の移動です。本セミナーは、粘土表面科学の権威である Cliff Johnston 教授（アメリカパデュー大学；元アメリカ粘土学会長）の来日にあわせて開催する特別セミナーです。この問題に関心のある方の参加を歓迎します。（呼びかけ責任者：溝口勝＠農学国際専攻）

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Chemistry
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Professional Positions
Los Alamos National Laboratory, Postdoctoral Fellow (1983 – 1985)
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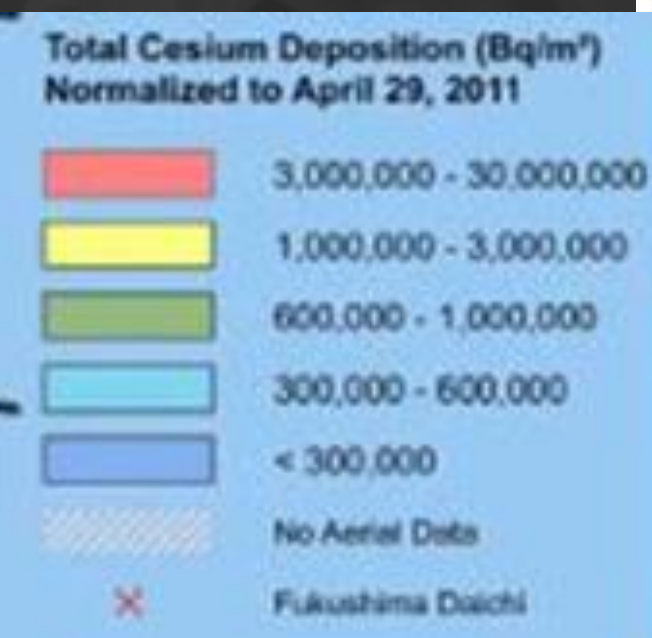
Asst.-Assoc Professor (1985 – 1993)
Los Alamos National Laboratory, Sabbatical Fellow (1991)
Katholieke Universtiet Leuven, Belgium, Sabbatical (1992 and 2002)
Purdue University, Department of Agronomy,
Assoc. Professor - Professor (1993 – present)

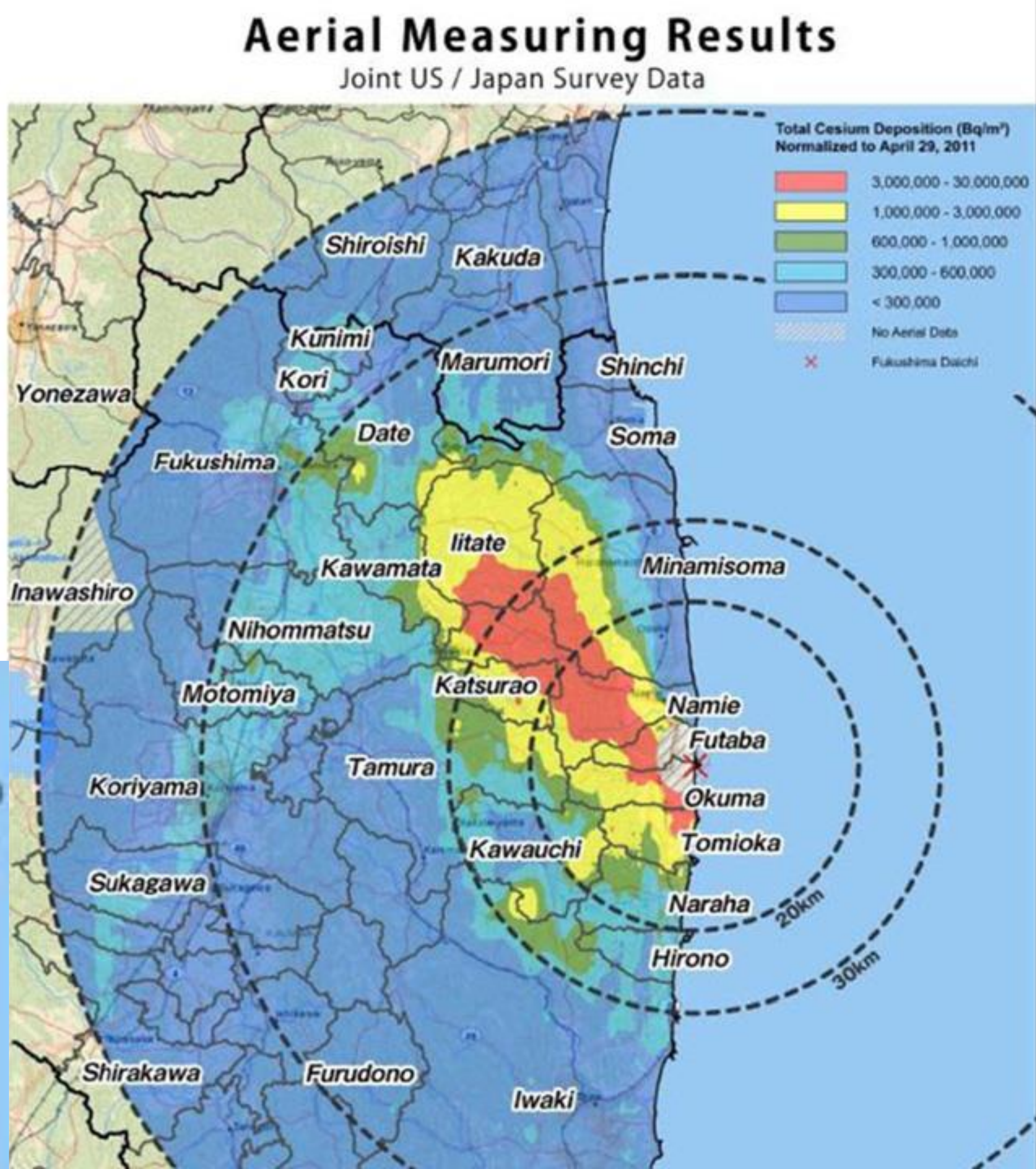
Membership in Academic, Professional and Scholarly Societies
American Chemical Society / Clay Minerals Society / Mineralogical Society of America / Soil Science Society of America

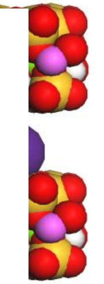
お問合わせ アグリコクーン 産学官民連携室
TEL:03-5841-8882
e-mail: office@agc.a.u-tokyo.ac.jp

Data collected on April 30, 2011

Presented on May 30, 2013







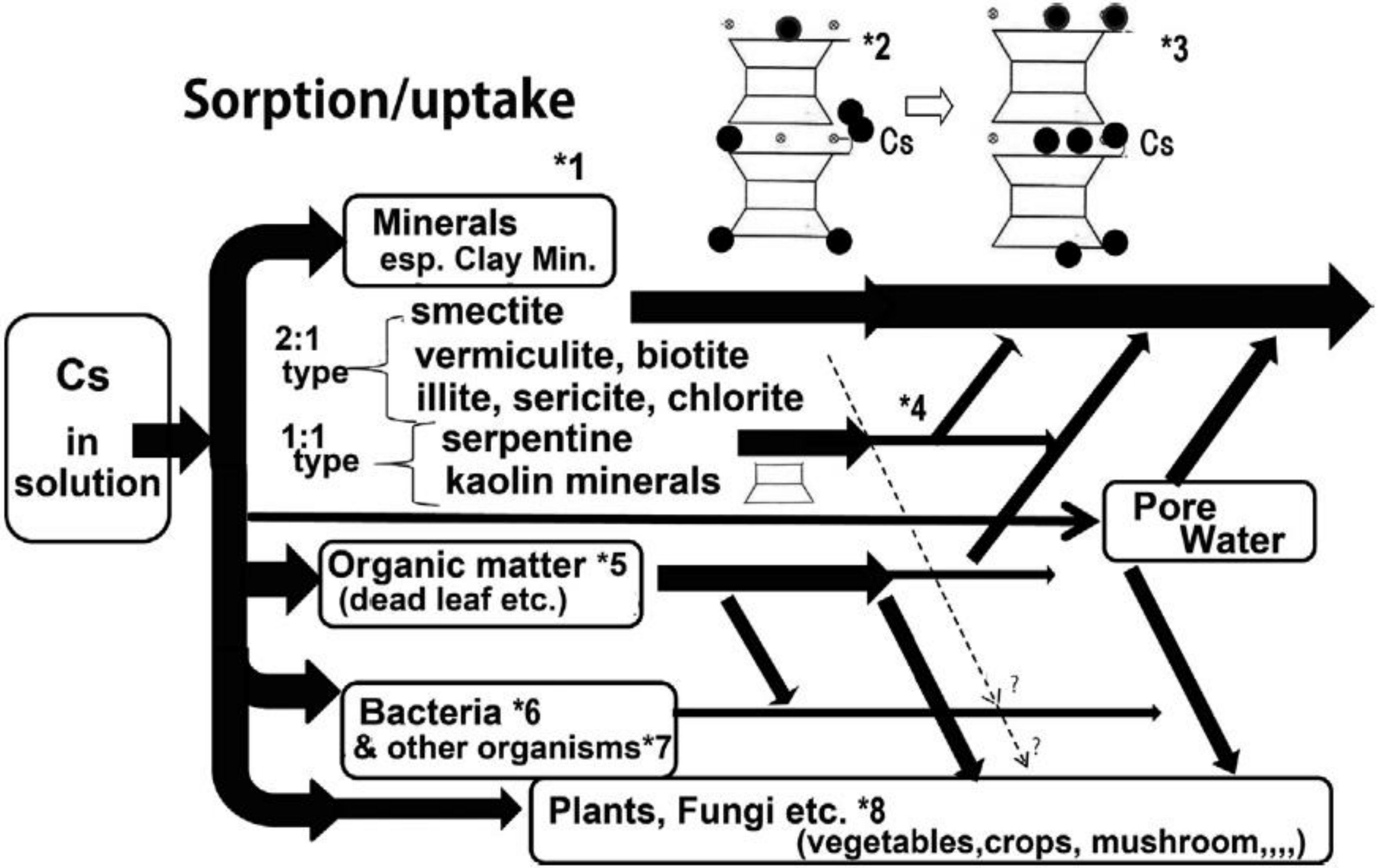
Heavy Metals in the Environment

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

Yasunori Mahara*

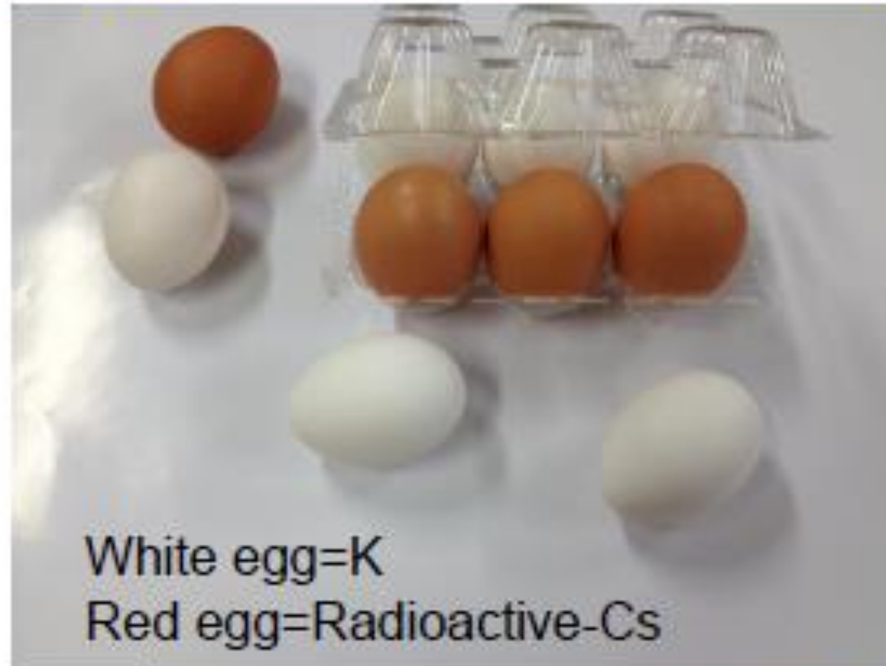
- The vertical migration of ^{90}Sr and ^{137}Cs produced by the explosion of the atomic bomb in 1945 was investigated in an unsaturated soil layer in the of Nagasaki.
- **The in situ migration rates of ^{90}Sr and ^{137}Cs were estimated to be 4.2 mm/yr and 1.0 mm/yr, respectively, when the rate of movement of soil water was 2500 mm/yr.**
- The in situ Kd values were calculated to be 300 and 1200 *L*/kg, respectively.
- These are probably the only results that exist for the interaction between soil and ^{137}Cs and ^{90}Sr over 40 yr.

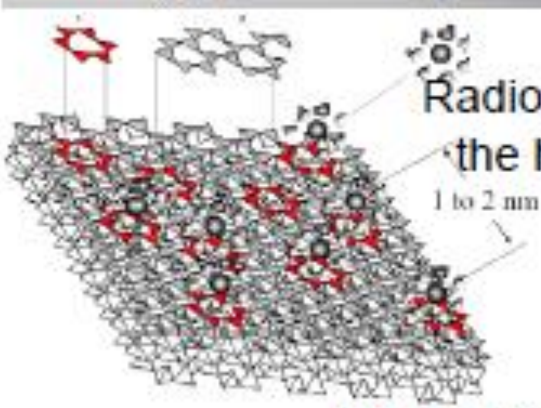
Y. Mahara. Storage and Migration of Fallout Sr-90 and Cesium-137 for Over 40 Years in the Surface Soil of Nagasaki. *J. Env. Qual. 22 (4):722-730, 1993.*



J. Akai, N. Nomura, S. Matsushita, H. Kudo, H. Fukuhara, S. Matsuoka, and J. Matsumoto. Mineralogical and geomicrobial examination of soil contamination by radioactive Cs due to 2011 Fukushima Daiichi Nuclear Power Plant accident. *Physics and Chemistry of the Earth 58-60:57-67, 2013.*

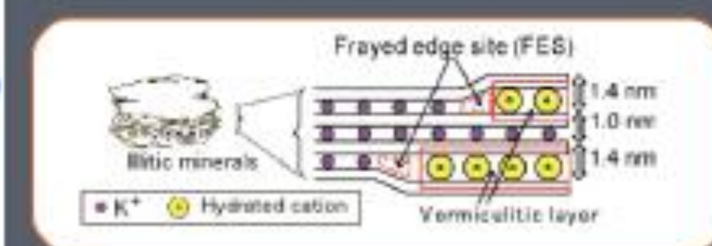
Radioactive-Cs is replaced with K and fixed to the clay particles



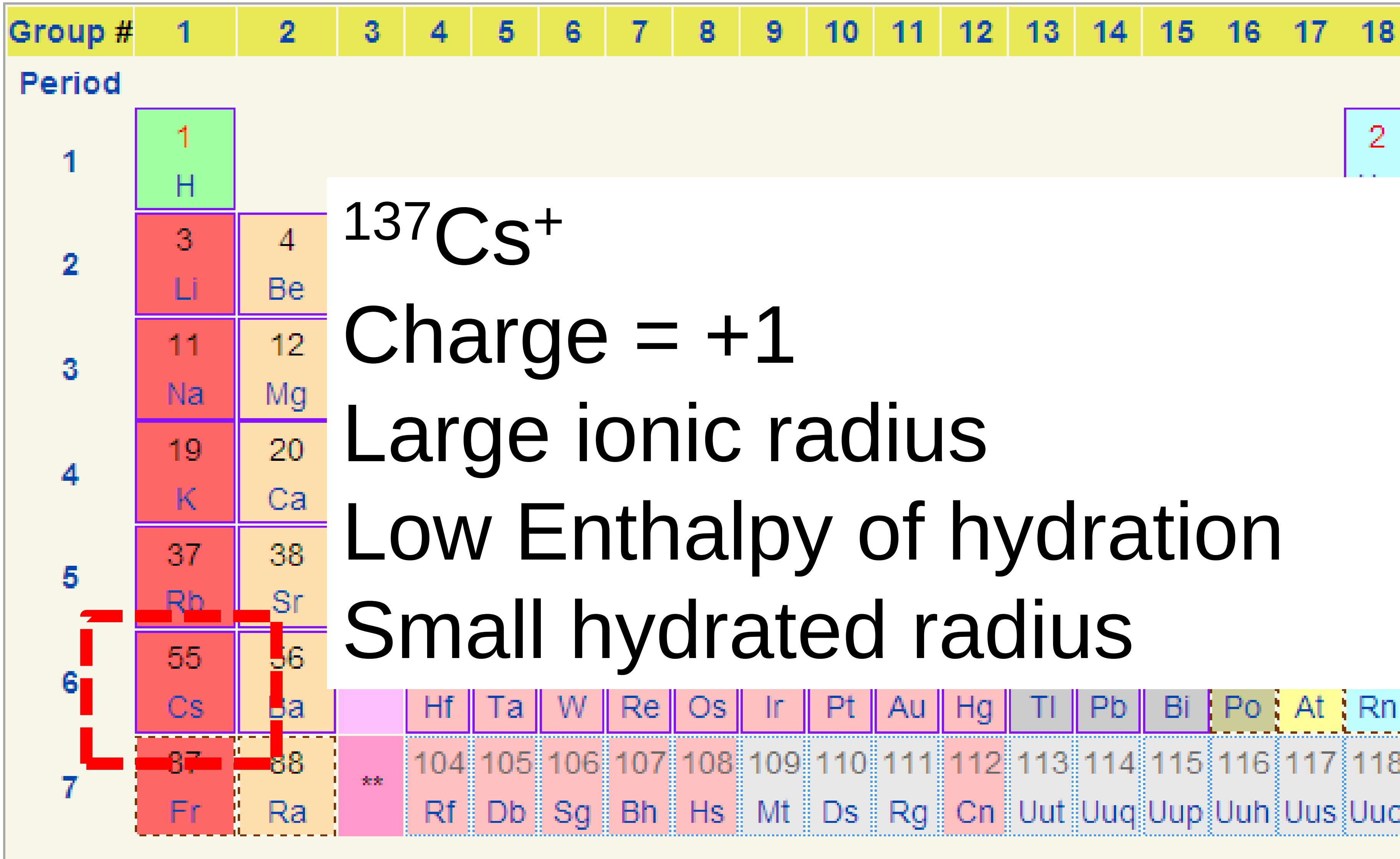


Radioactive-Cs is dropped into the hole in the clay surface!

by Prof. C.T Johnston @Purdue Univ.



RIP(Radiocesium Interception Potential)
(Cremers et al., 1988 in Nature)



$^{137}Cs^{+}$

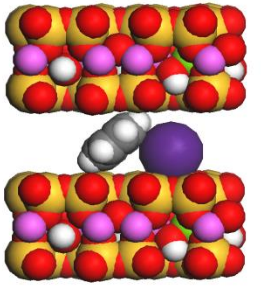
Charge = +1

Large ionic radius

Low Enthalpy of hydration

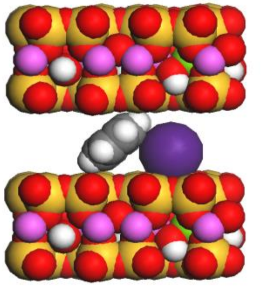
Small hydrated radius

Molecular Approaches to study Cs-clay interactions related to Fukushima (partial)



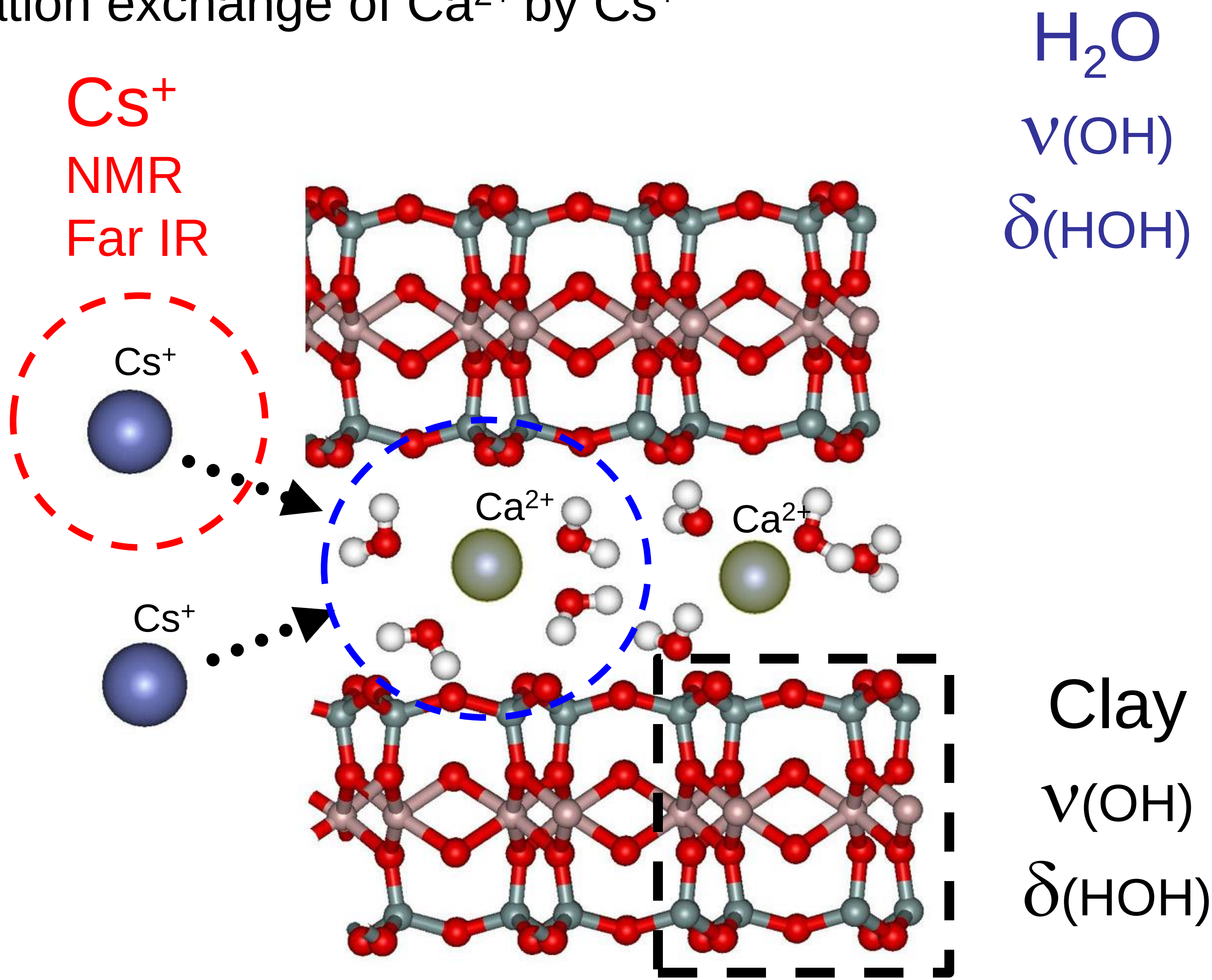
- SEM, TEM and related methods (T. Kogure[*])
- Autoradiography (J. Akai et al)
- Positronium Lifetime Spectroscopy (K. Sato)
- NMR (K. Sato et al)
- Sorption / Desorption
- Far IR

In Situ ATR-FTIR study of cation exchange reactions on smectite



- ATR FTIR sensitive to changes in interfacial/interlayer water
- Water molecules closely linked/organized by the exchangeable cations present
- Up until recently most of our work focused on Li, Na, K, Mg and Ca. What happens with clays are exchange with Cs?

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



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$_{Na\text{-}SWy2}$)

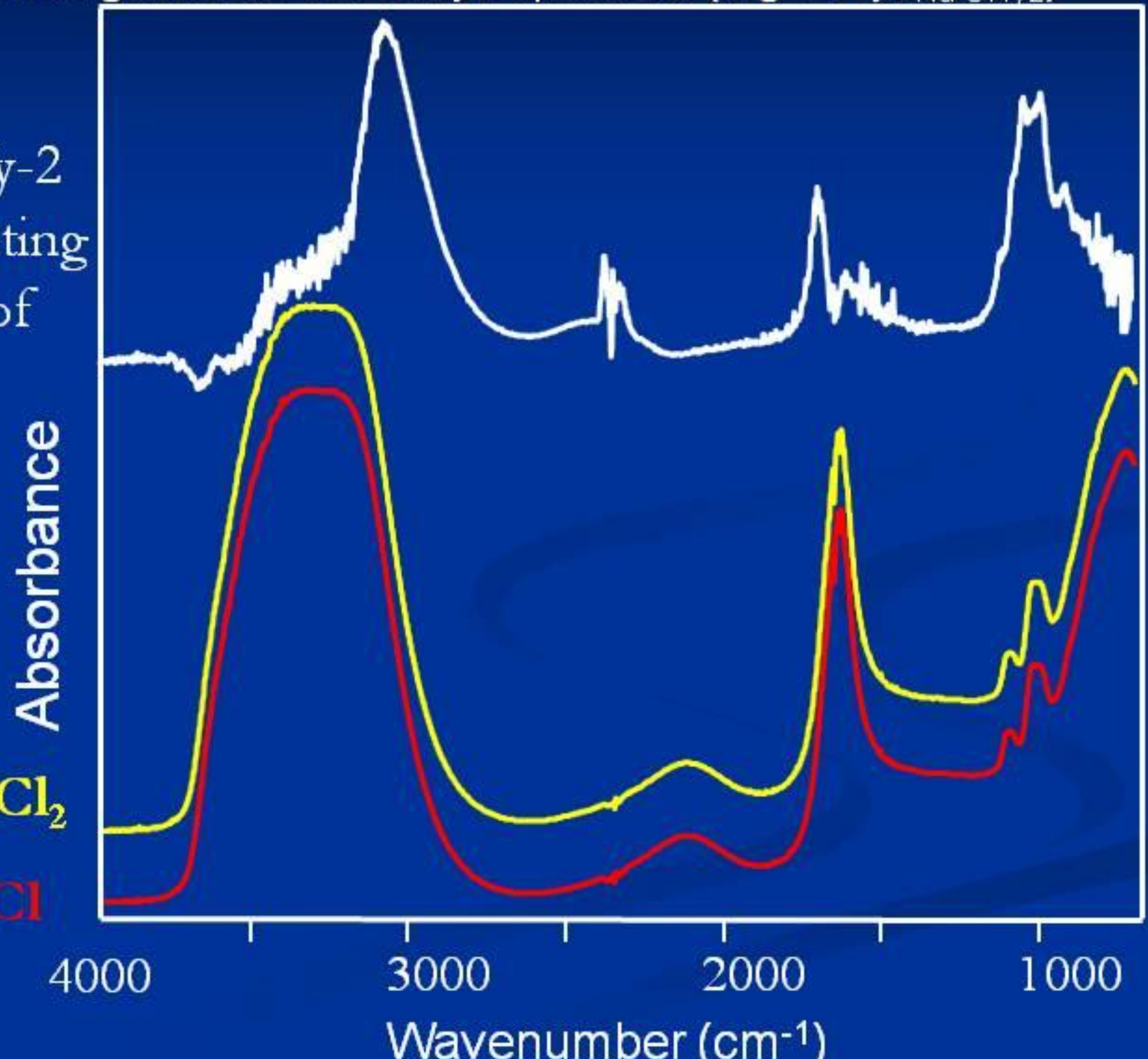
C = B – A

Mg-SWy-2 – Na-SWy-2

Spectral changes resulting from the exchange of Mg^{2+} for Na^{+}

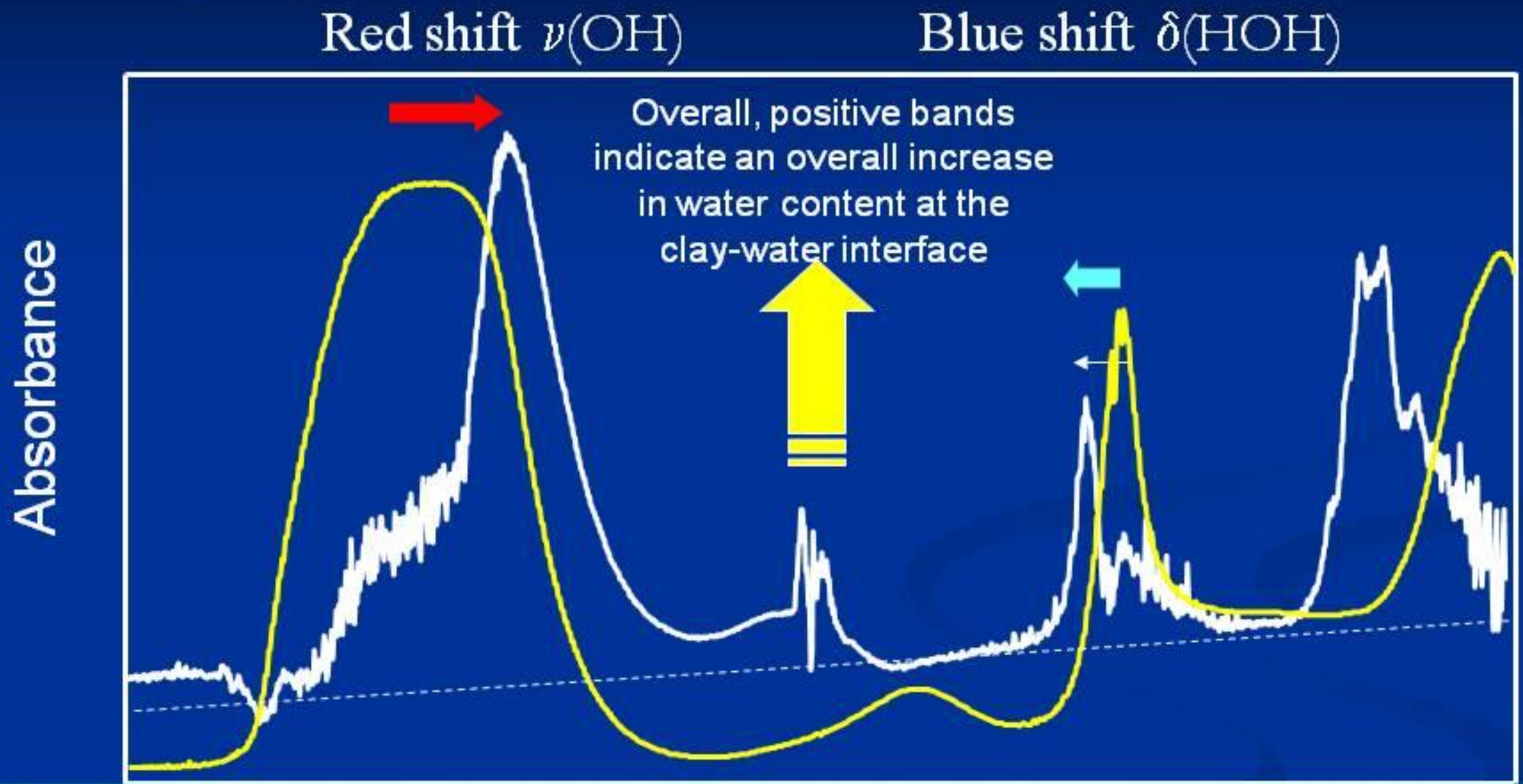
B: clay + 0.1 M $MgCl_2$

A: clay + 0.1 M NaCl

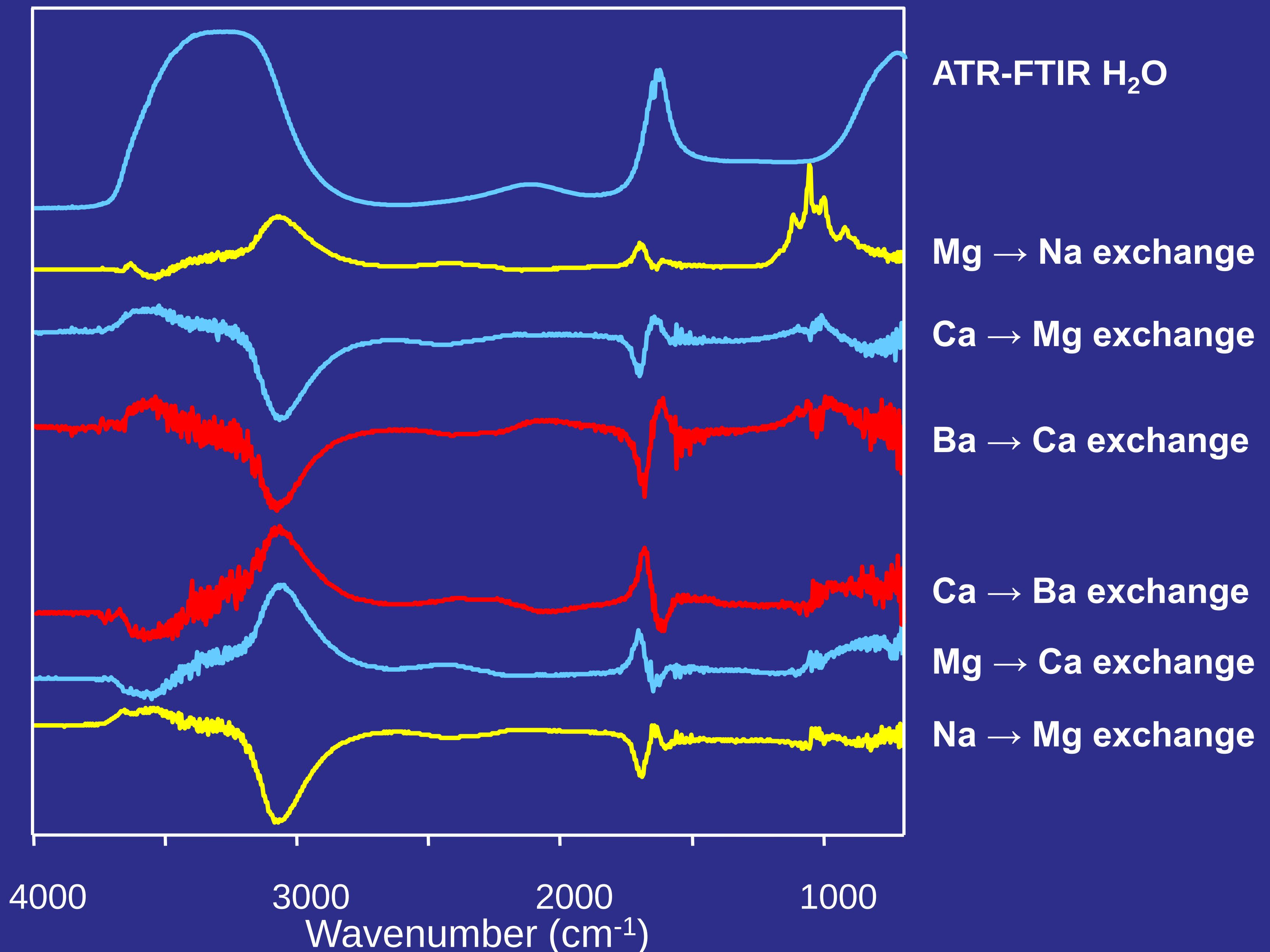


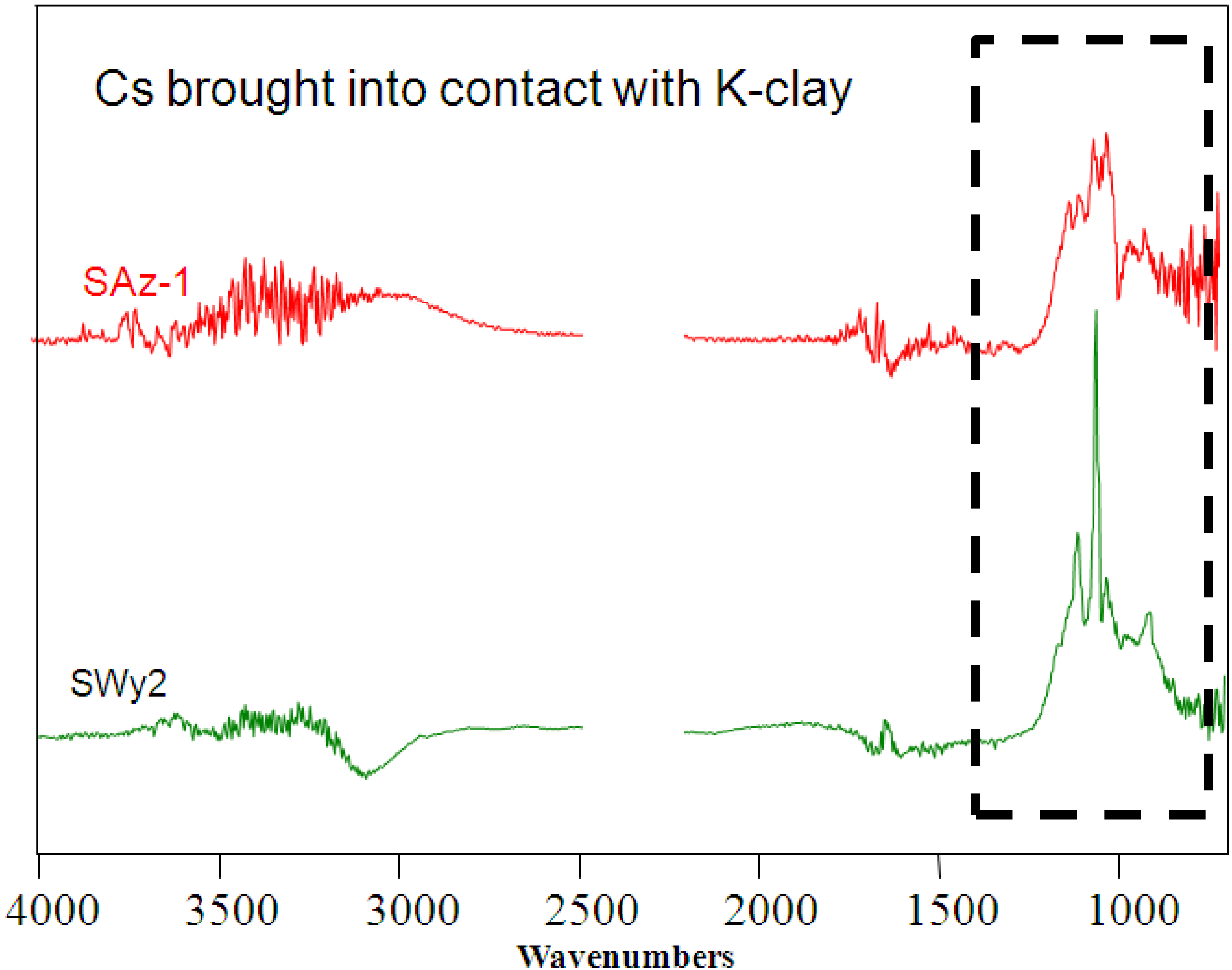
Mg → Na exchange

Comparison: FTIR Mg-SWy2$_{Na\text{-}SWy2}$ spectrum (white) to the ATR-FTIR spectrum of bulk water (yellow)



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


ATR-FTIR H_2O
Mg → Na exchange
Ca → Mg exchange
Ba → Ca exchange
Ca → Ba exchange
Mg → Ca exchange
Na → Mg exchange
4000
3000
2000
1000
Wavenumber (cm^{-1})


Cs brought into contact with K-clay
SAz-1
SWy2
4000
3500
3000
2500
2000
1500
1000
Wavenumbers

Summary

- ATR-FTIR sensitive to detect changes of interfacial water. Reproducible changes for two references clays and four soil clays
- Changes consistent with hydration enthalpies of cations
- This method provides a direct method to study the interaction of Cs with siloxane ditrigonal cavity and the interlayer fixation that occurs.
- Potential for Hofman-Klemen fixation with heating?
- Incredibly complex, difficult problem. At the same time, however, Japan has consistently been a leader in the clay / soil science frontiers with significant intellectual resources.

Acknowledgements

- Collaborators:
  - Steve Agnew, Steve Boyd, Brian Teppen, Hui Li
- Students and postdocs
  - Bushra Khan, Kiran Rana, Kamol Dad
- Funding sources: NSF, EPA, NIH and USDA