PAUL SCHERRER INSTITUT

Nuclear Energy and Safety Research Department
Laboratory for Waste Management

Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut
Rainer Dähn

Validation of uptake processes of radionuclides such as Cs on clay minerals by EXAFS

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Outline

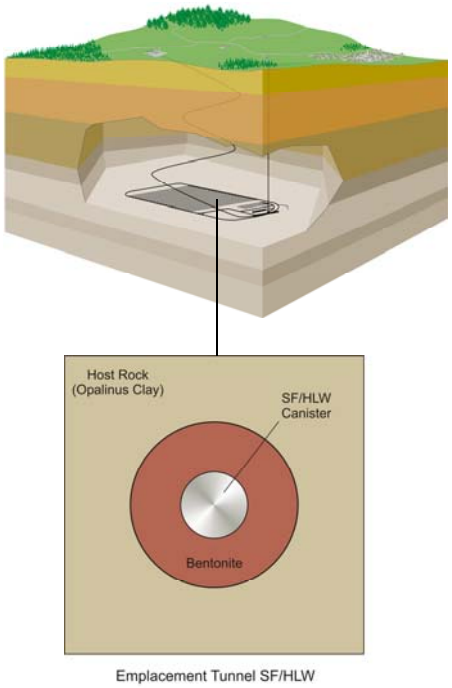
- Introduction
- Validation of uptake mechanisms as function of aqueous chemistry by:
  - Characterization of solid phases
  - Conventional EXAFS and polarized EXAFS modeling
  - Molecular modeling approach
- Status of Cs research at PSI
- Potential for quantitative modeling
- Potential role to support Fukushima challenges
- Conclusions

Geological waste repository concept

- Engineered and natural barrier materials to retard RN transport into the environment
  - Backfill material **bentonite** consists **75% montmorillonite**
- Molecular-level understanding of chemical processes (sorption, redox, dissolution)
  - Modeling mobility of radionuclides
  - Development and validation of sorption models

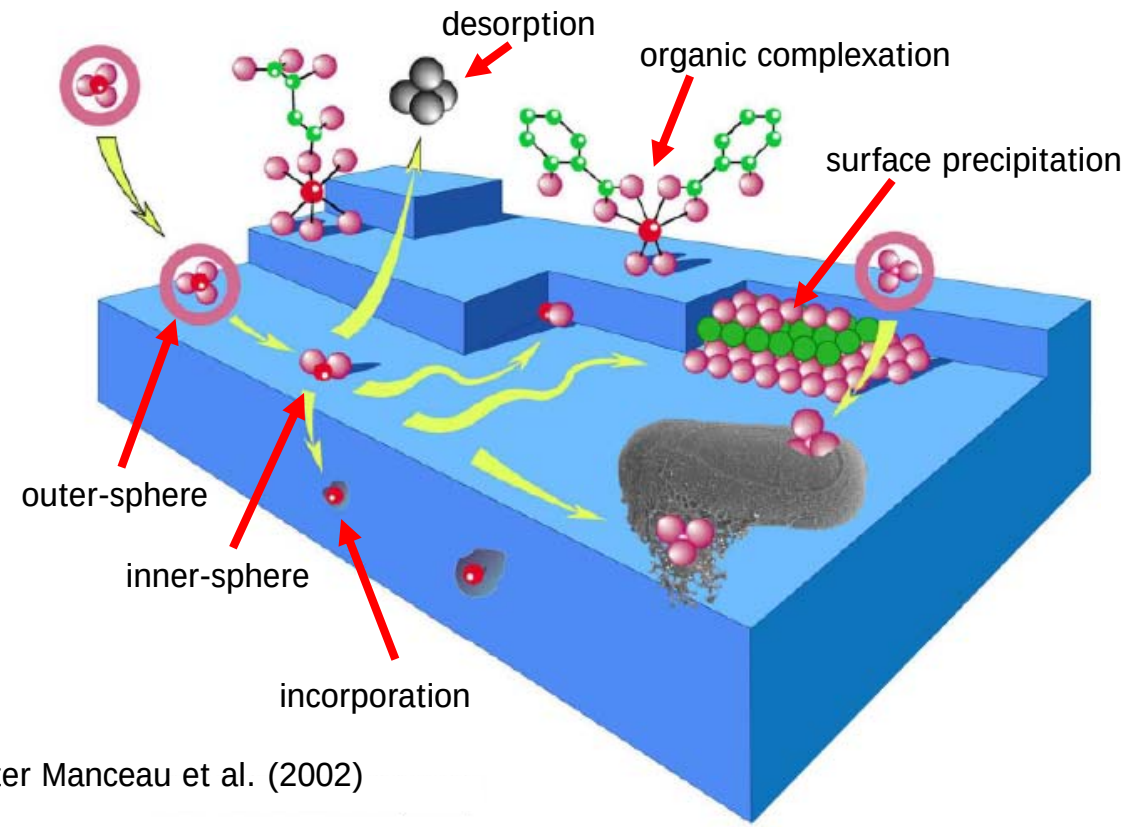
e.g. high level waste repository

NAGRA NTB 02-05



Emplacement Tunnel SF/HLW

Uptake mechanisms



After Manceau et al. (2002)

Approach

Investigations of predominant mineral phases:

- Wet chemistry
  - Development of sorption models
  - Input for XAFS measurements

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- Bulk XAFS (powder and P-EXAFS)
  - Structural information (oxidation state, coordination numbers, bond distances, system disorder)
  - Determination of uptake processes
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  - Input for sorption models and molecular modeling

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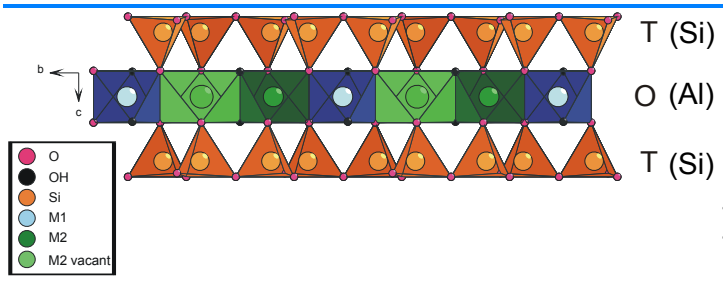
Investigations of heterogeneous samples:

- Micro-XRF, Micro-XAS and Micro-XRD techniques
  - Determination of reactive phases
  - Identification of newly formed phases
  - Speciation along diffusion profiles

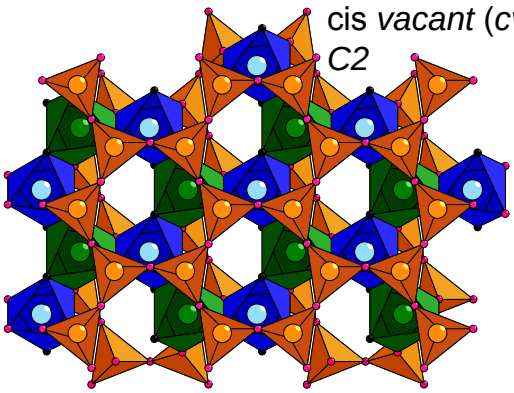
2:1 clays e.g. vermiculite + montmorillonite



T (Si)

O (Al)

T (Si)



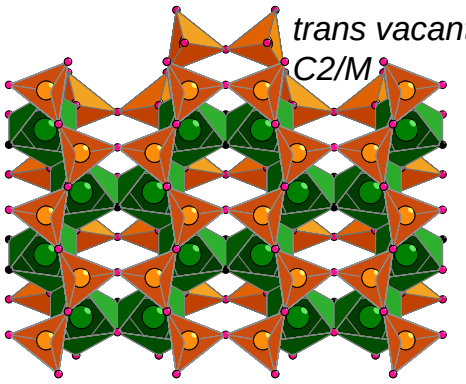
cis *vacant* (*cv*)
C2

Montmorillonite:

- dioctahedral clay
- trans sites (M1) and cis sites (M2)
- predominant cis vacant
- up to 2 mmol/kg Zn incorporated

Why Zn:

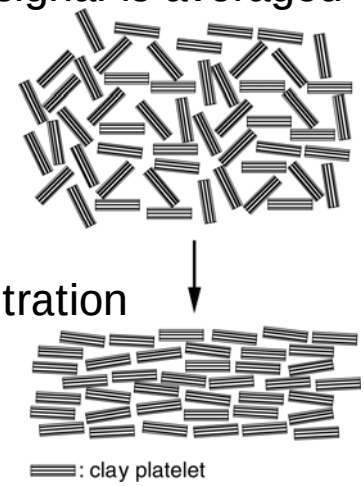
- Is an analogue for ^{63}Ni
- Allows to measure down to 2 mmol/kg in the presence of 1 wt% Fe
- Zn contamination from smelters, mining, industrial and municipal waste



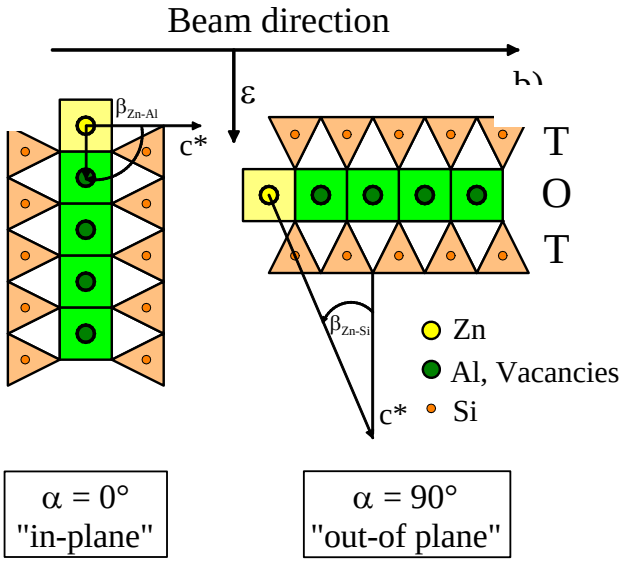
trans vacant (*tv*)
C2/M

Polarized EXAFS

Problem: Powder-EXAFS signal is averaged



➢P-EXAFS on highly oriented self-supporting clay films



α = 0° "in-plane"

α = 90° "out-of plane"

Increased sensitivity to distinguish between IS/OS complexes, important for Cs uptake by clays

Conventional vs. MM based EXAFS modelling

	Conventional	MM based
Bond Distance:	Fitting parameter	Fixed by MM
Coordination:	Fitting parameter	Fixed by MM
Disorder:	Fitting parameter	Fitted/Fixed by MM
Multiple Scattering:	Can be considered	Full account

Flowchart for conventional EXAFS modelling

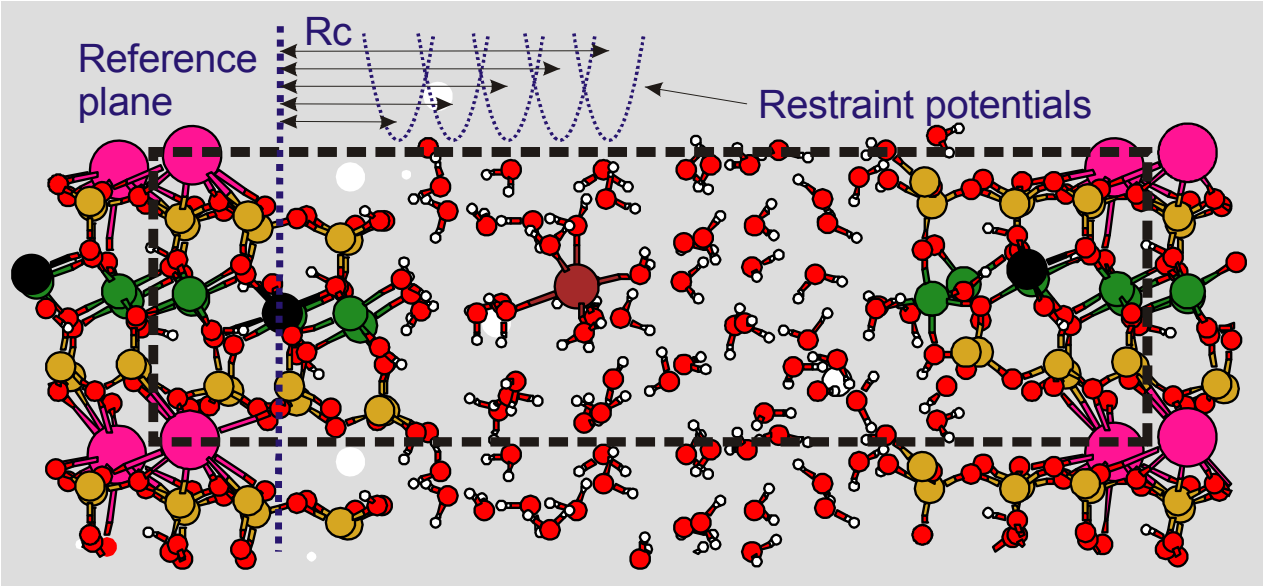
1. Measured spectra
2. Shell model fit (Inter-atomic distances and coordination)
3. What are the structures consistent with Inter-atomic distances?

Flowchart for MM based EXAFS modelling

1. MM modeling of potential structures
2. Calculate EXAFS spectra based on structures from MM modeling
3. Linear fit of calculated EXAFS spectra to measured ones

Both approaches should give consistent results !

Case study: molecular simulations of Zn uptake

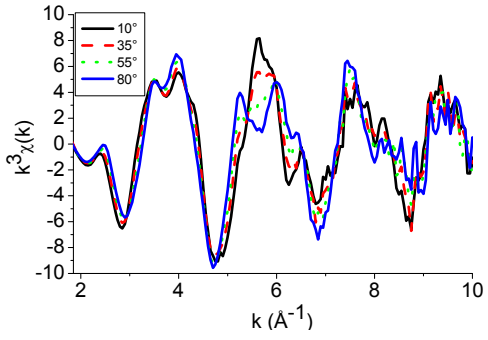


- ab initio molecular dynamics and geometry optimization using CP2K -package
- Meta-dynamics with classical Force Fields CLAYFF
  - Zn-Al and Zn-Si coordination number
- System composition $K_2Mg_2Al_{10}Si_{24}O_{60}(OH)_{12} \times 56H_2O \times Zn^{2+}$
- System dimensions 10.44×28.5×10.0 Å

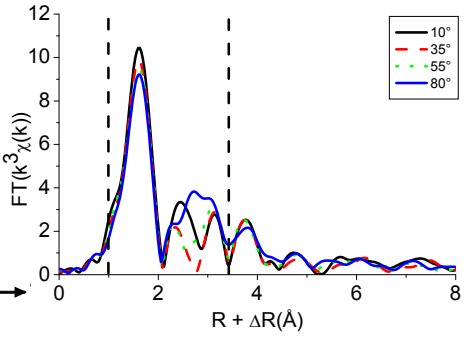
Characterisation of the solid phase

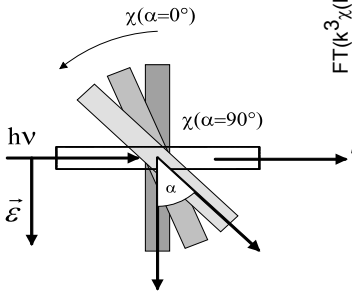
P-EXAFS: Zn incorporated in montmorillonite (MILOS)

Measured data

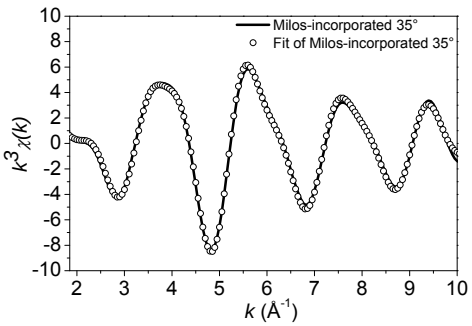


Fourier transformed data





FT^{-1}



Data were fitted using theoretical phase and amplitude function (FEFF) for Zn-O, Zn-Al and Zn-Si backscattering pairs

Dähn et al., GCA 2011

P-EXAFS data modelling

P-EXAFS: Zn incorporated in montmorillonite (MILOS)

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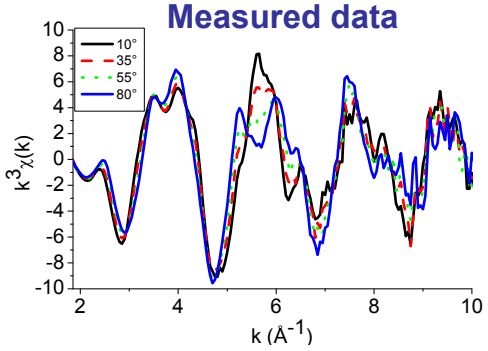
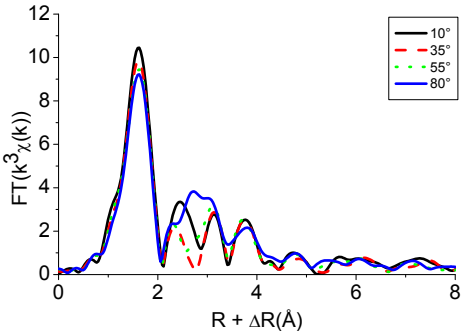


Fourier transformed data



Shell	CN	R_{ij}
Zn-O	6.4(4)	2.07(1)
Zn-Al	3.3(6)	3.02(2)
Zn-Si	4.0(6)	3.22(2)

P-EXAFS data modelling

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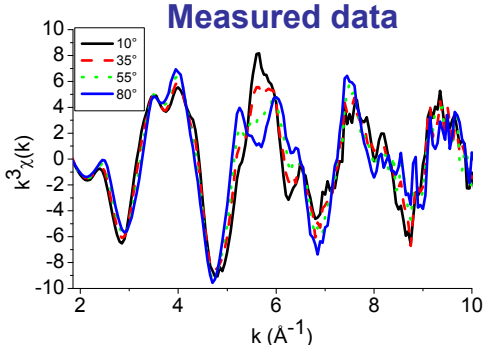
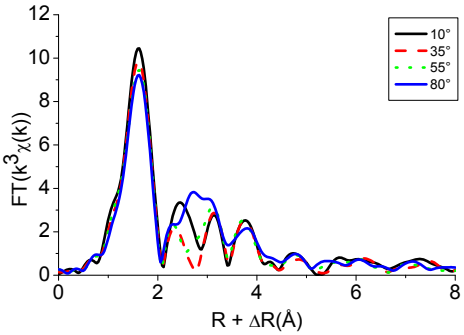


Fourier transformed data



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$CN_{Zn\text{-}Al} \sim 3$

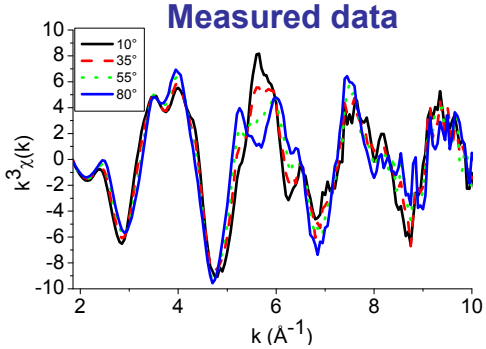
Zn is NOT filling empty octahedral positions

In that case: $CN_{Zn\text{-}Al} \sim 6$

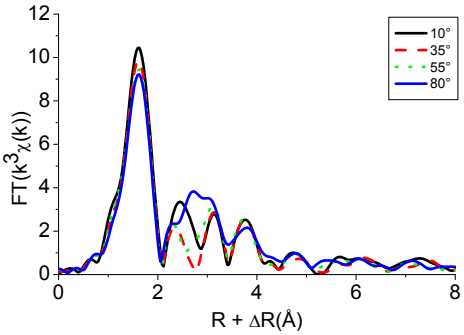
P-EXAFS data modelling

P-EXAFS: Zn incorporated in montmorillonite (MILOS)

Measured data



Fourier transformed data



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Zn-O	6.4(4)	2.07(1)
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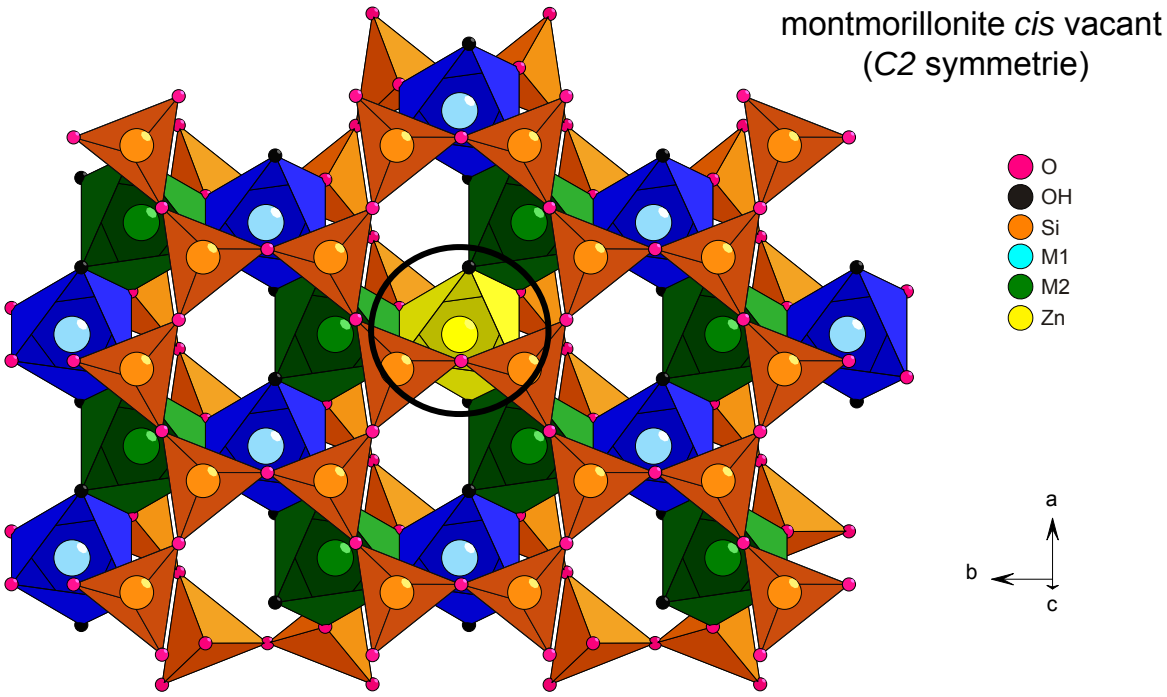
Only one Si distance

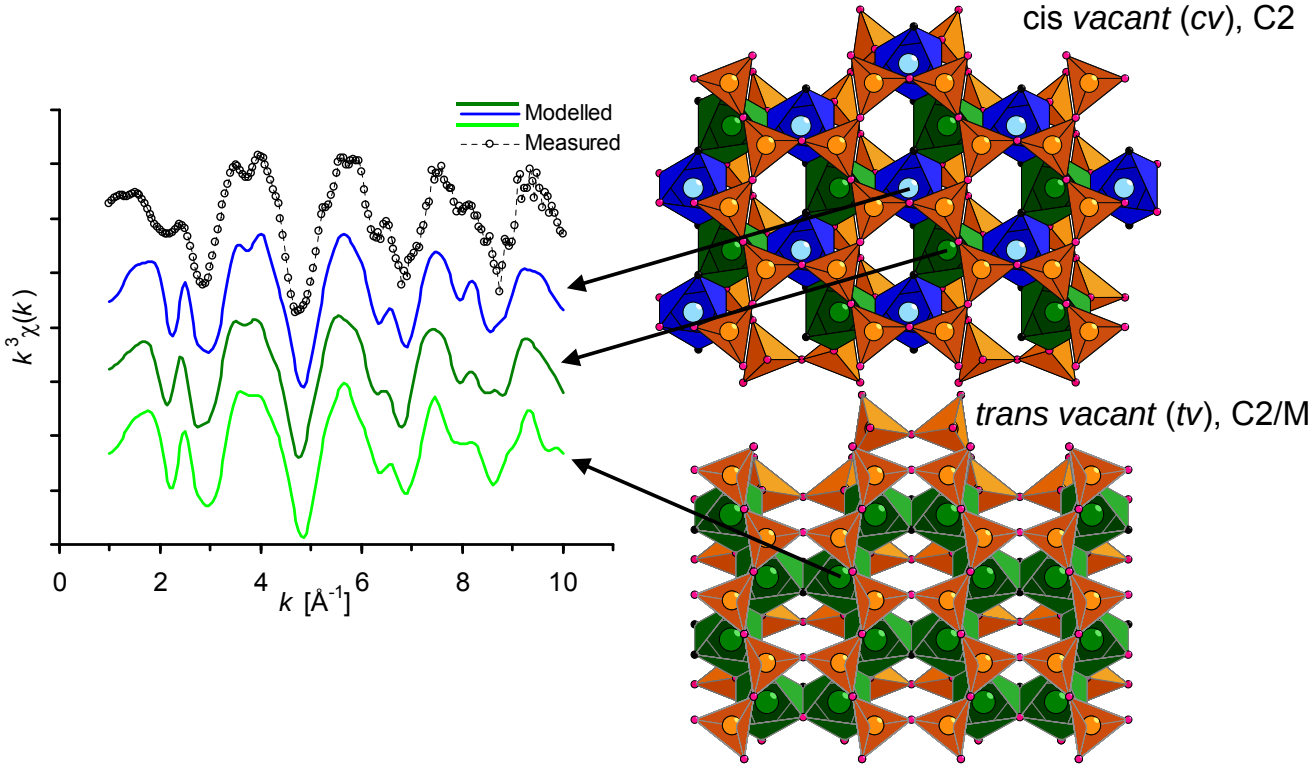
Zn is in trans positions

Zn incorporated in montmorillonite

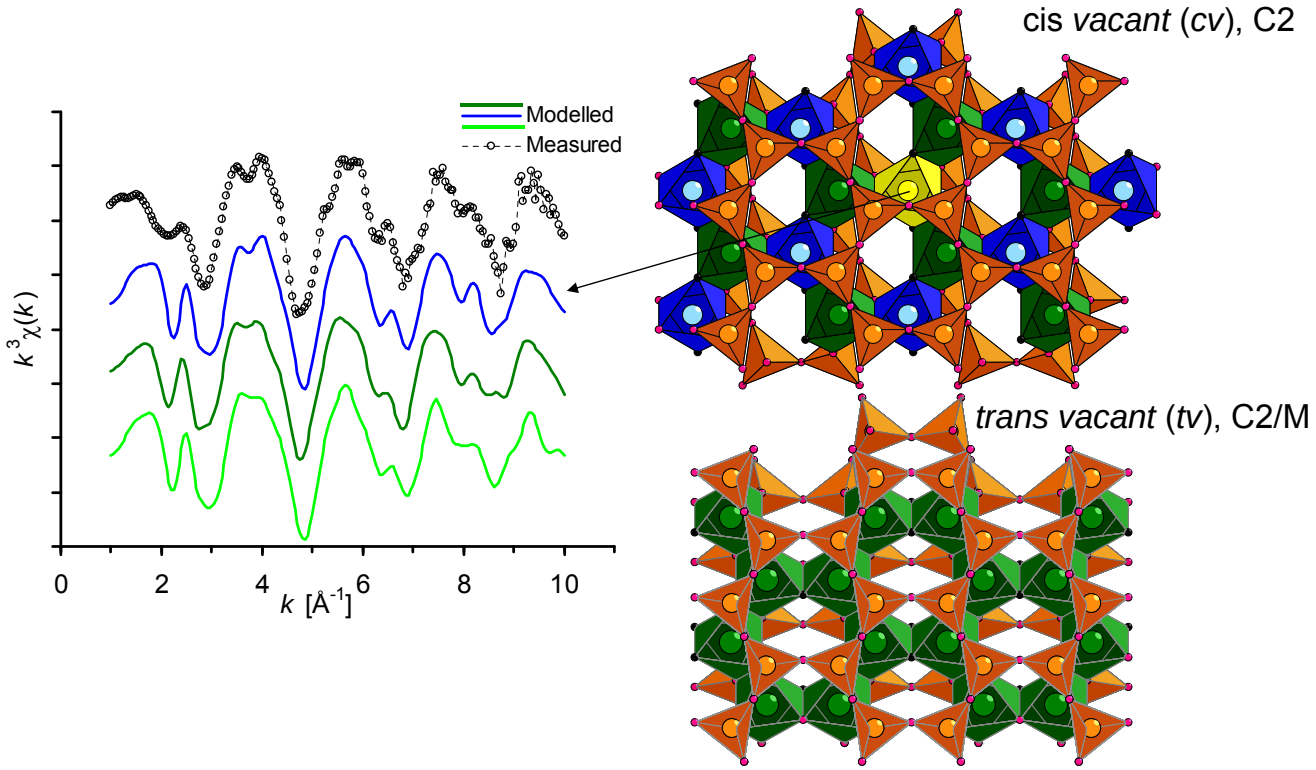


Zn is incorporated into montmorillonite trans sites

Zn incorporated in montmorillonite



Zn incorporated in montmorillonite

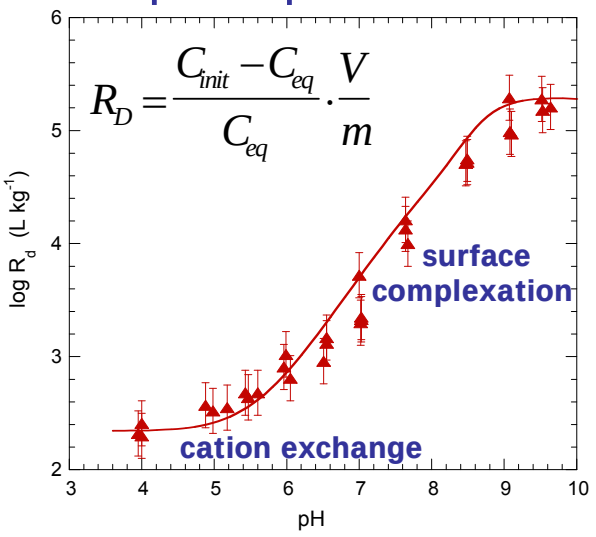


Zn is incorporated to *cv*-montmorillonite into *trans* sites

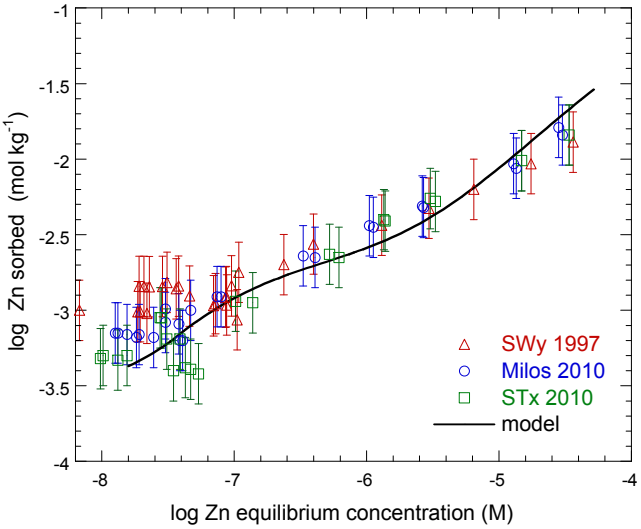
Validation of uptake mechanisms

Zn uptake by montmorillonite (0.2 M $NaClO_4$)

pH dependent

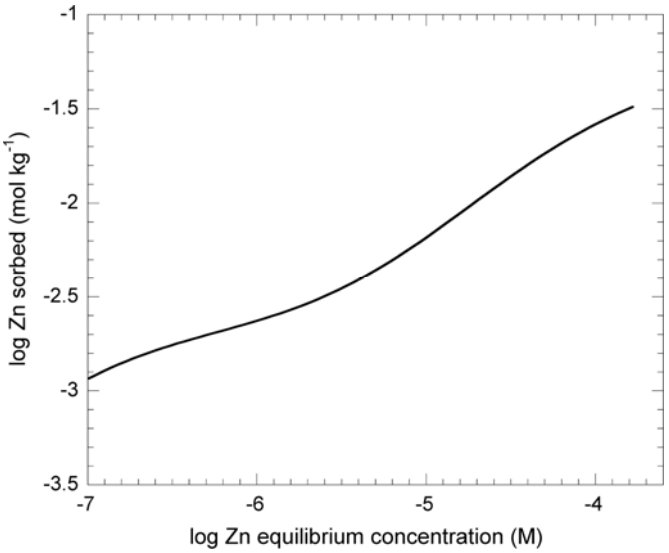


isotherm (pH 7.0)



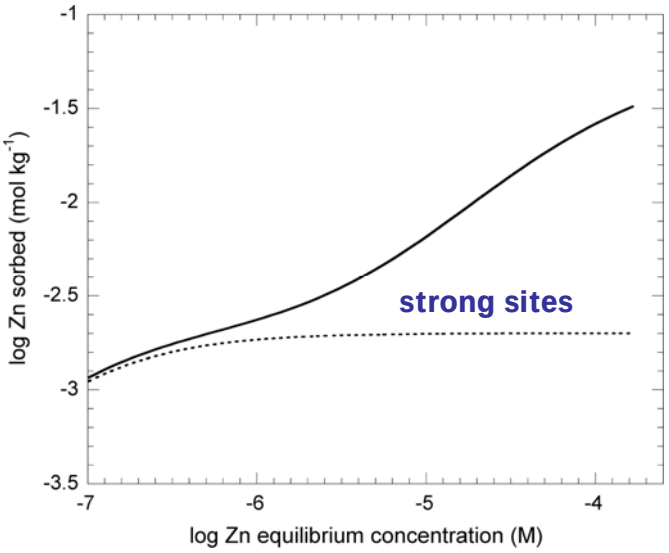
2SPNE SC/CE sorption model

2SPNE SC/CE = **2** **s**ite **p**rotolysis **n**on **e**lectrostatic **s**urface **c**omplexation and **c**ation **e**xchange
(Bradbury M. H. and Baeyens B., J. Contam. Hydrol. 1997)



Strong sites

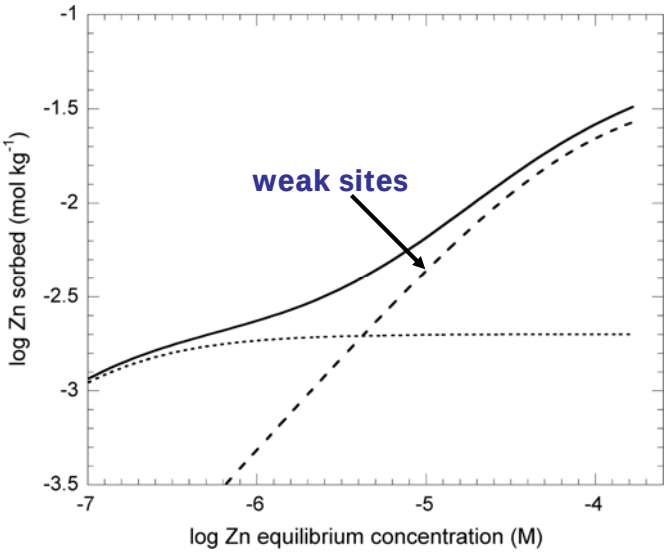
2SPNE SC/CE = **2** site **p**rotolysis **n**on **e**lectrostatic **s**urface **c**omplexation and **c**ation **e**xchange



"strong": <2 mmol/kg capacity

Weak sites

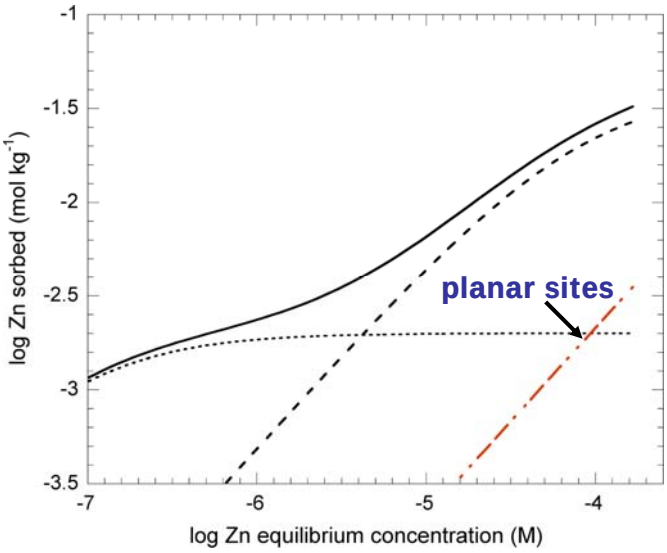
2SPNE SC/CE = **2** site **p**rotolysis **n**on **e**lectrostatic **s**urface **c**omplexation and **c**ation **e**xchange



"weak": <40 mmol/kg capacity

Planar sites

2SPNE SC/CE = **2** site **p**rotolysis **n**on **e**lectrostatic **s**urface **c**omplexation and **c**ation **e**xchange



planar sites play a role:
- **low pH**
- **low ionic strength**
- **at high loadings**

Planar sites

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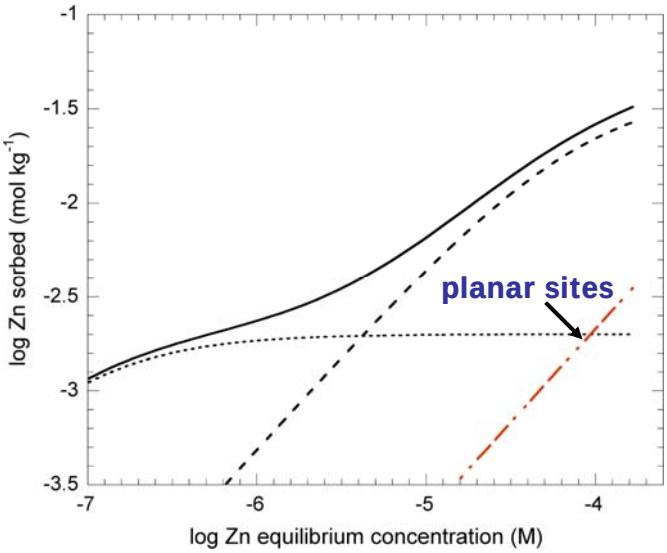


planar sites play a role:
- **low pH**
- **low ionic strength**
- **at high loadings**

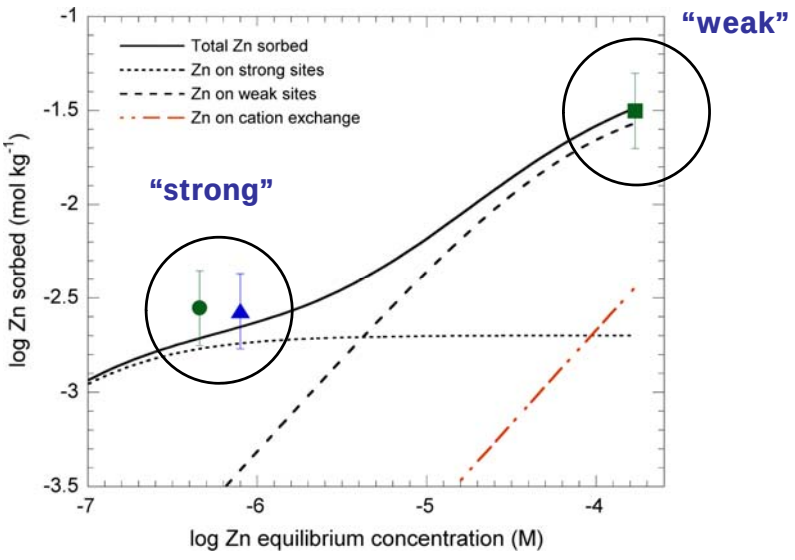
in this study:
pH 7
0.2 M $NaClO_4$
2-40 mmol/kg

Strong/weak sites?

Main question:

Do the "strong" and "weak" sites have a crystallographic / physical meaning, or are they just fit parameters?

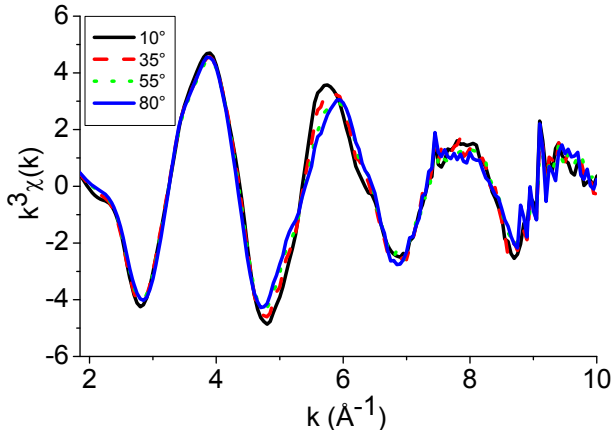
Preparation of EXAFS samples

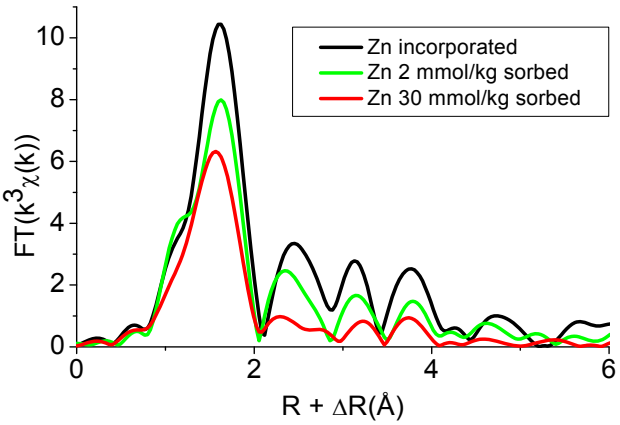


Model is used to design the experiment and find favourable conditions for "strong" and "weak" sites

Zn uptake at medium absorber concentration

30 mmol/kg Zn sorbed to STX-1





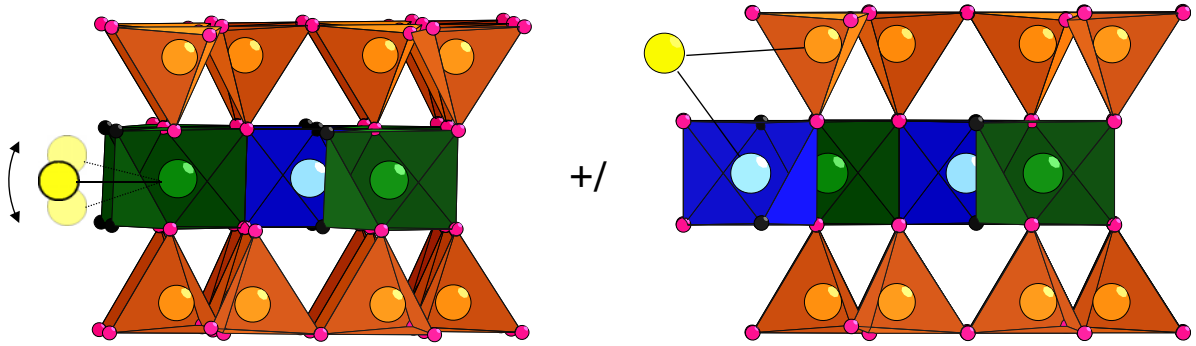
Shell	CN	R_{ij}
Zn-O	~5.5	2.05
Zn-Al	~1.0	3.04
Zn-Si	~1.0	3.33

RSF peaks decrease with increasing loading:

- higher disorder
- complexes are sorbed close to β = 54.7°

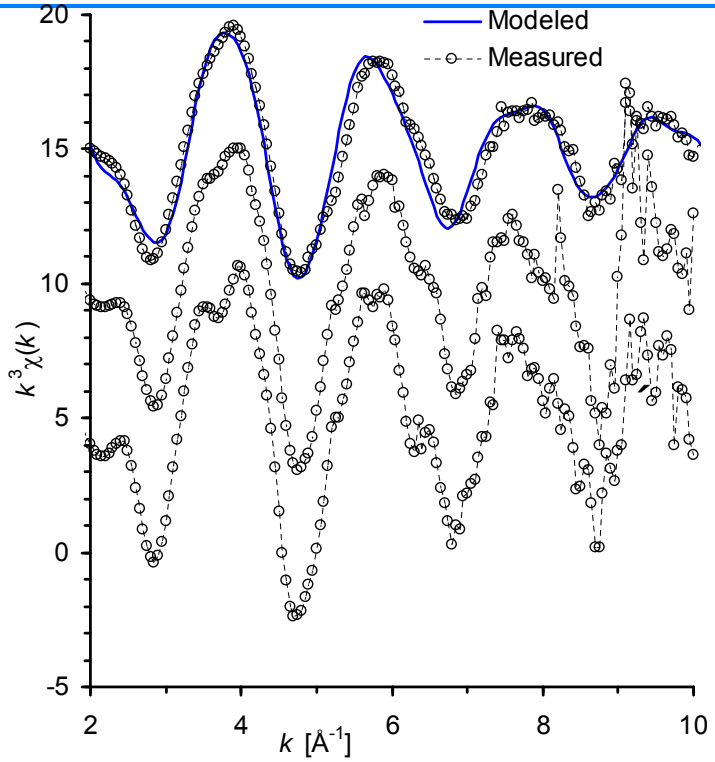
Zn uptake at medium absorber concentration

30 mmol/kg Zn sorbed to STX-1



P-EXAFS is unable do determine the predominant uptake mode => molecular modeling

EXAFS data fitting at medium loadings (weak sites)



Texas $\equiv S^W$ ***Zn***

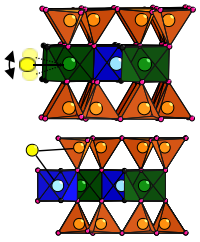
Texas $\equiv S^S$ ***Zn***

Milos $\equiv S^S$ ***Zn***

Best Fit ***Texas*** $\equiv S^W$ ***Zn***

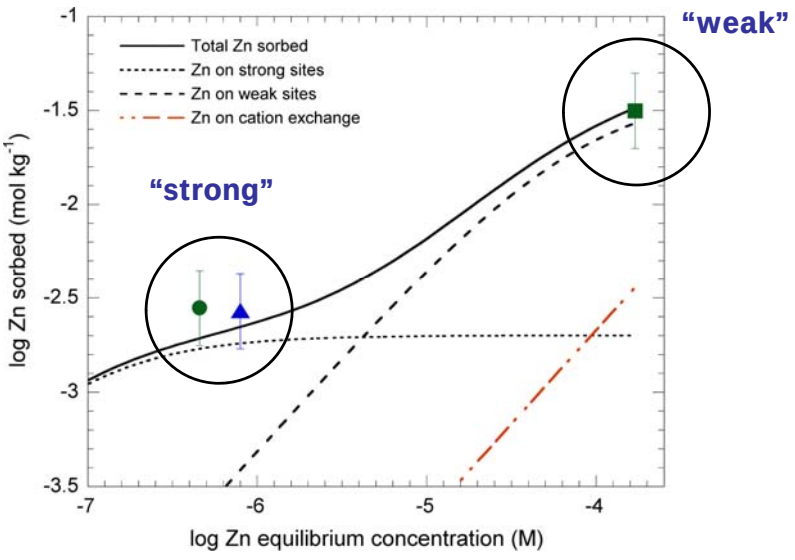
40% (010)
61% (110)

0% (xxx)
101% Total



Modeled structures can only explain uptake at low loadings!

Preparation of EXAFS samples

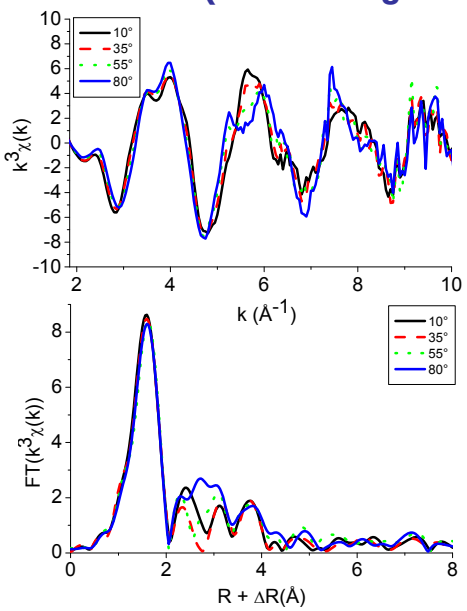


Model is used to design the experiment and find favourable conditions for "strong" and "weak" sites

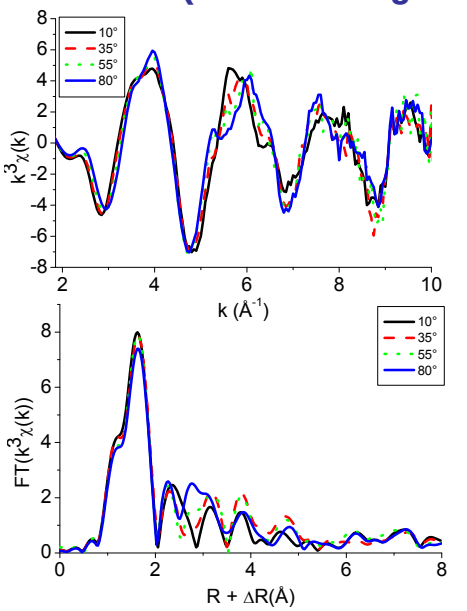
Zn uptake at low absorber concentrations

2 mmol/kg Zn sorbed to Milos and STX-1

Milos (2 mmol/kg inc.)



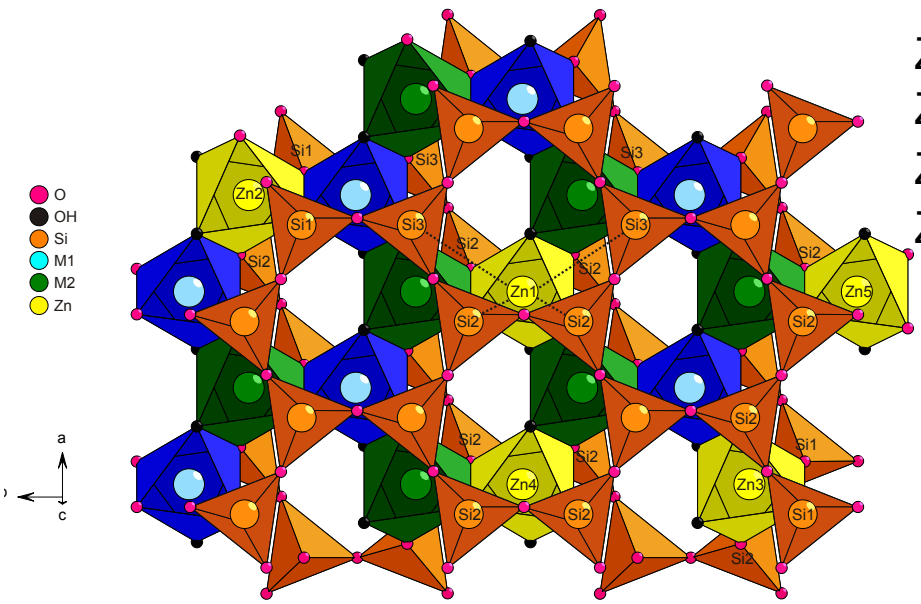
STx-1 (0.2 mmol/kg inc.)



Strong P-EXAFS dependency

Zn uptake at low absorber concentrations

2 mmol/kg Zn sorbed to Milos and STX-1

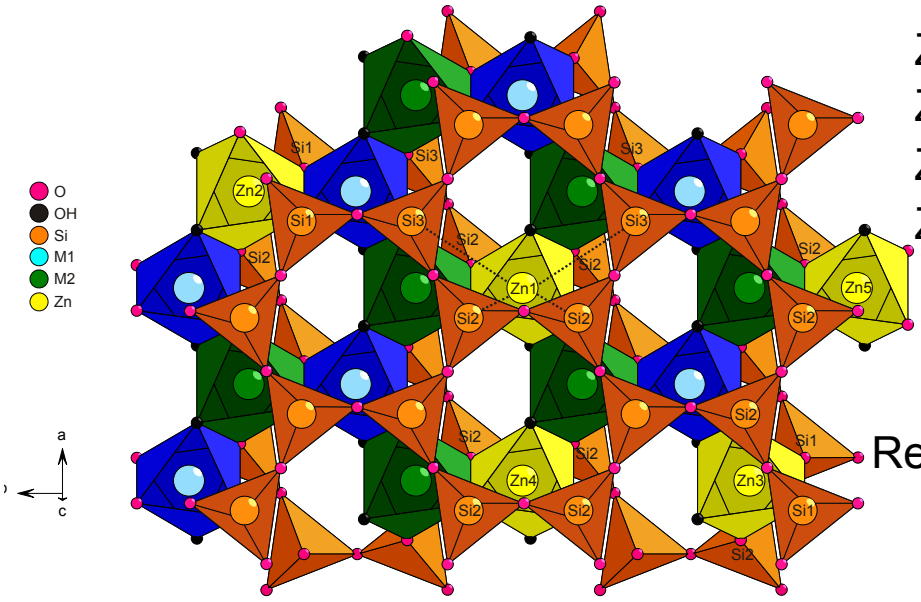


Shell	CN	R_{ij}
Zn-O	~5.5	2.05
Zn-Al	~1.5	3.02
$Zn\text{-}Si_1$	~1.0	3.06
$Zn\text{-}Si_2$	~2.2	3.26

two Si distances

Zn uptake at low absorber concentrations

2 mmol/kg Zn sorbed to Milos and STX-1



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Zn-O	~5.5	2.05
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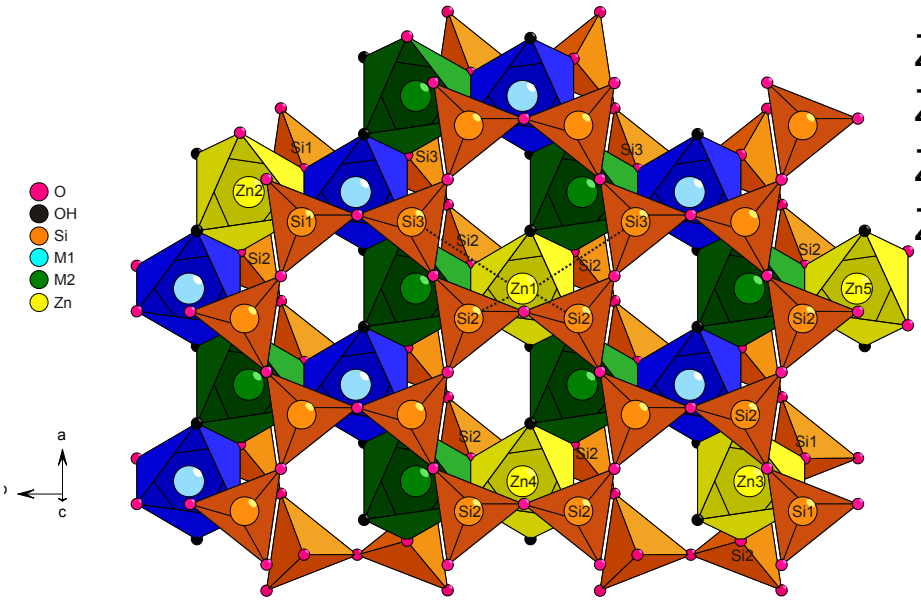
Zn-Si_2	~2.2	3.26

Reduced Coordination Numbers

Zn uptake at low absorber concentrations

2 mmol/kg Zn sorbed to Milos and STX-1



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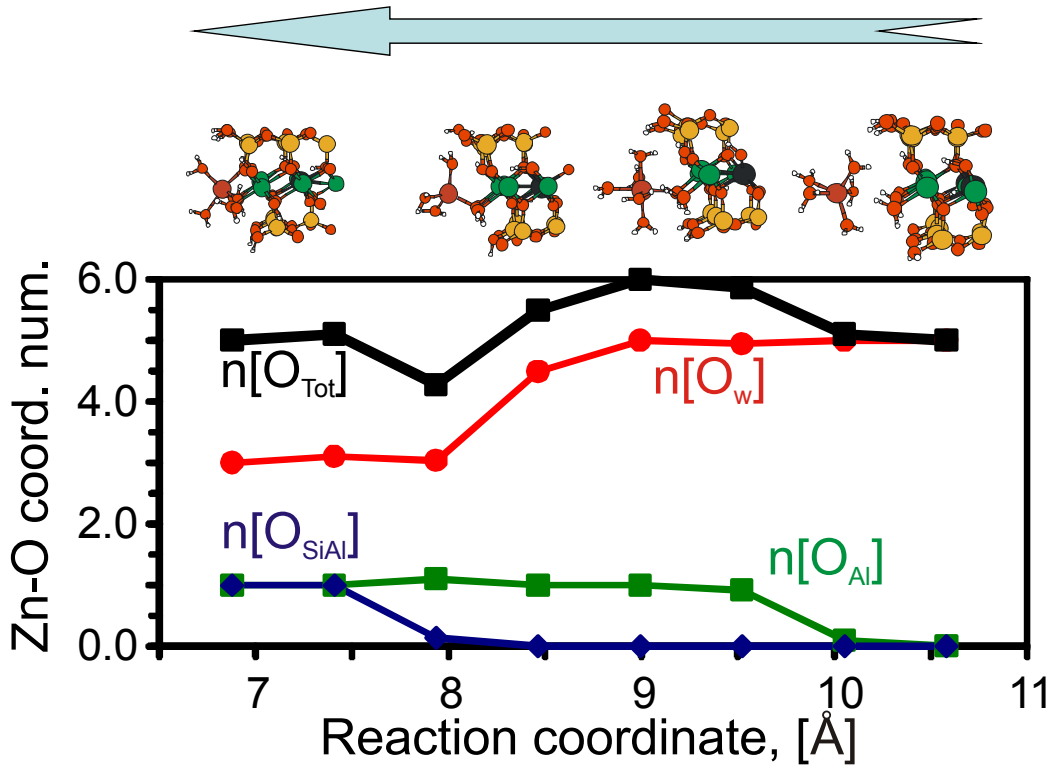
Dähn et al., GCA 2011

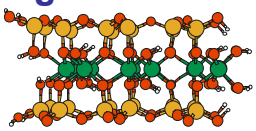
Mixture of cis- and trans-like edge sites

Sorption from solution at (110) surface



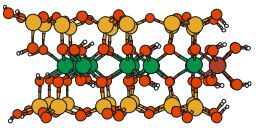
Structure search for sorption sites

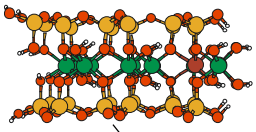
Edge surfaces



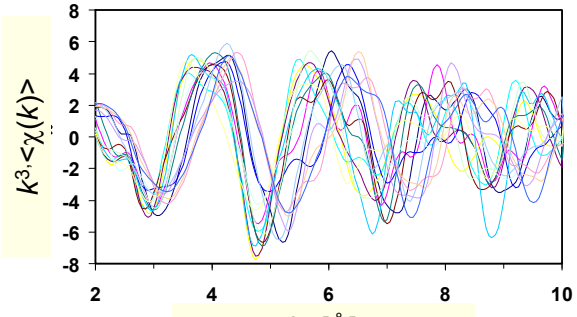
cv- and *tv*-(010), (110), (130), (110)

Substitutions



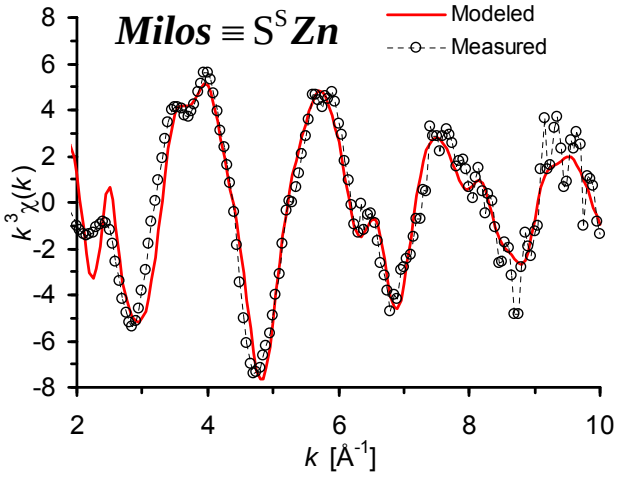


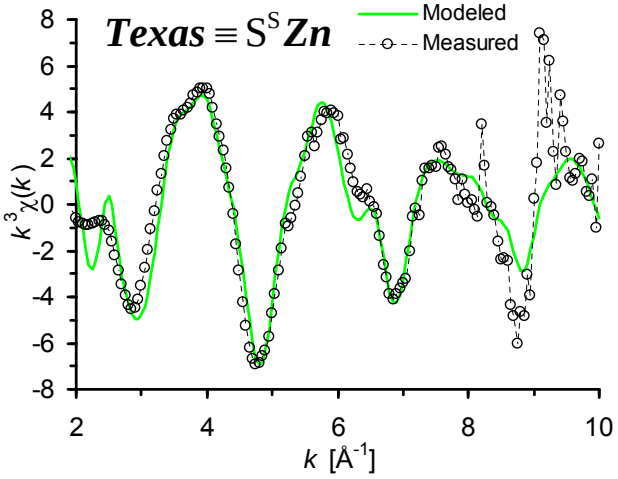
cv-(010)-Zn^{T}, *cv*-(010)-Zn^{C} ,
tv-(010)-Zn^{C}, …



$$\left\| k^3 \left(\sum_i a_i^2 < \chi(k) >_i - \chi^{exp}(k) \right) \right\|^2 + \left\| a_i^2 \right\|^2 \Rightarrow \min$$

EXAFS data fitting at low loadings (strong sites)



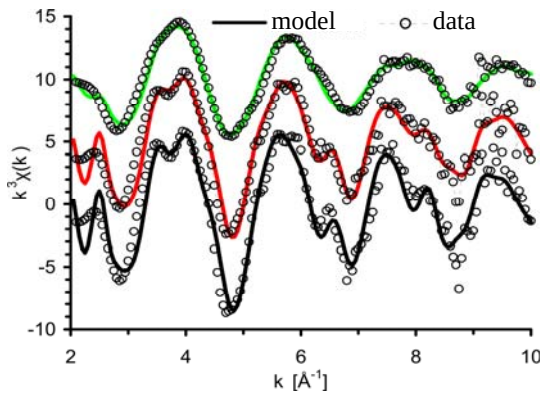


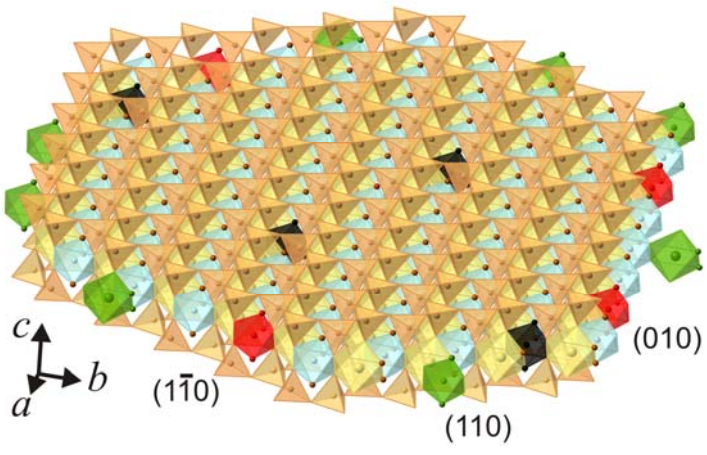
cv-(010)-ZnT	25%
cv-(110)-ZnT	27%
~~cv-Bulk -ZnT~~	~~50%~~
Total	102%

cv-(010)-ZnT	42%
cv-(110)-ZnT	50%
~~cv-Bulk -ZnT~~	~~10%~~
Total	102%

Comparison EXAFS vs. MM

	CN_O	R_{ZnO}	CN_{Al}	R_{ZnAl}	CN_{Si1}	R_{ZnSi1}	CN_{Si2}	R_{ZnSi2}
Texas ≡ S^S*Zn*	5.1/6.0	2.05/2.12	1.1/2.1	3.02/3.08	1.3/0.6	3.06/3.08	2.1/2.6	3.26/3.28
Milos ≡ S^S*Zn*	6.0/6.0	2.05/2.11	1.5/2.5	3.02/3.06	1.2/0.8	3.10/3.11	1.5/2.8	3.26/3.27
Milos ≡ Zn^{inc}	6.4/6.0	2.07/2.10	3.3/3.0	3.02/3.05			4.0/4.0	3.22/3.22





Churakov S. V. and Dähn R. ES&T 2012

Good agreement between molecular modeling and EXAFS

Summary

- **“low” and “medium” Zn(II) loadings show different uptake behaviours.**
- **At low loadings, Zn(II) is structurally incorporated in octahedral edge positions.**
- **At medium loadings, the EXAFS spectra indicate that Zn(II) is sorbed as a mixture of inner-sphere complexes.**
- **This study confirms the assumption of the strong and weak site concept in the 2SPNE SC/CE sorption model.**
- **Molecular modeling can quantify uptake processes**

Status of Cs research at PSI

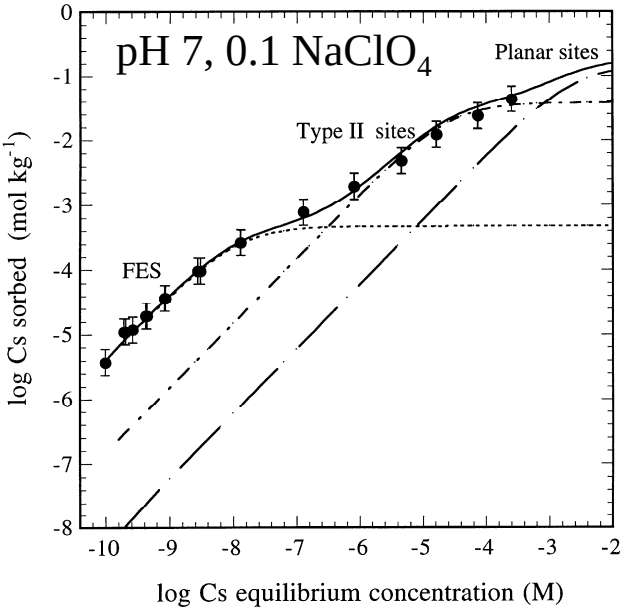
- Cs uptake by illite and argillaceous rocks
  - Wet chemistry and modeling ✓
  - Bottom-up approach ✓
  - EXAFS – in planning
- Cs diffusion in Opalinus Clay ✓
- Micro-spectroscopic studies of Cs uptake by Opalinus Clay
  - X-ray micro tomography ✓
  - microXRF and LA-ICPMS ✓

Potential for quantitative modelling

Generalised Cs model for illite (Bradbury & Baeyens, 2000)

To model the sorption isotherm on illite:

- 3 site types are required: Frayed Edge Sites (FES), Type II sites and Planar sites
- Selectivity coefficients of Cs with respect to other cations e.g. Na and K are required



Cs sorption model summary

Site type	Site capacity CEC illite = 200 meq kg^{-1}
FES	0.25 % of CEC
Type II	20 % of CEC
Planar	80 % of CEC

Cation exchange reaction	Log K_c
Na-FES + K ⇔ K-FES + Na Na-FES + Cs ⇔ Cs-FES + Na	2.4 7.0
Na-II + K ⇔ K-II + Na Na-II + Cs ⇔ Cs-II + Na	2.1 3.6

Boda Claystone Formation, Southern Hungary	Opalinus clay, Northern Switzerland
250 Ma	180 Ma
Deposition in a shallow lacustrine environment	Deposition in shallow marine environment
	
Depth ~1000 m	~ 500 m

Blind predictions of the sorption isotherms

Modelling constraints / assumptions:

- Generalised Cs and 2SPNE SC/CE sorption models for illite is also valid for muscovite (10 Å) and ilite/smectite mixed layers
- Site capacities scaled to the illite/muscovite and/or illite/smectite mixed layer contents
- Sorbing species: only free cations and hydrolysed species, no carbonate or other aqueous complexes
- Nagra/PSI 01/01 thermodynamic data base to calculate radionuclide speciation in the porewater
- No further adjustment of the model parameters *i.e.* no modification of surface complexation constants

Illustration of the "bottom-up" approach

U(VI) on Boda Claystone

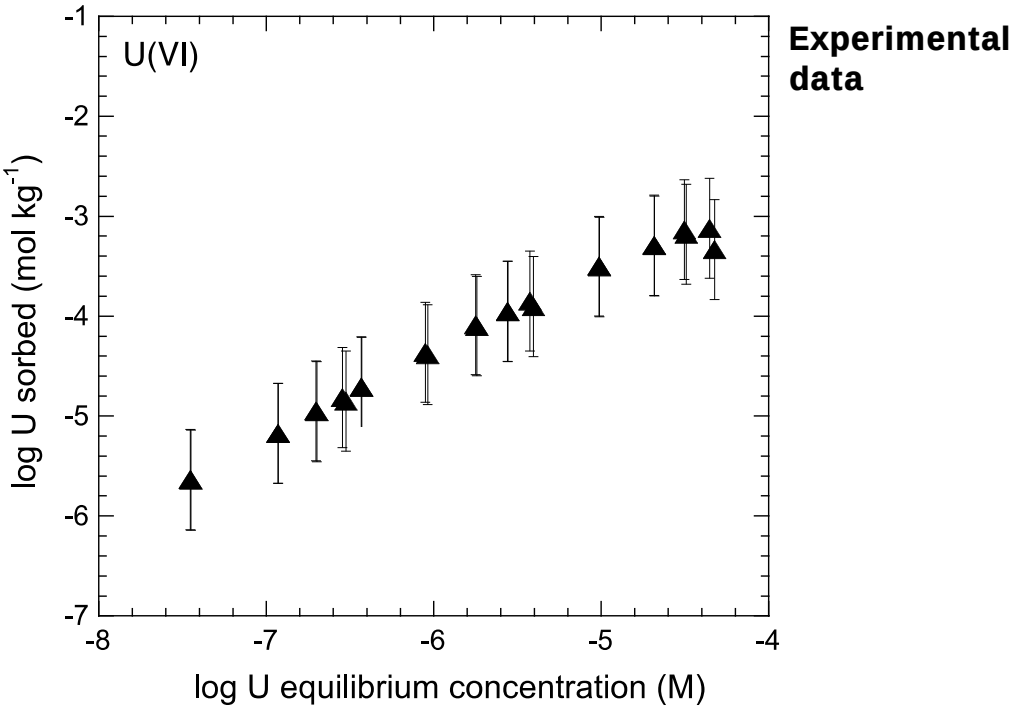
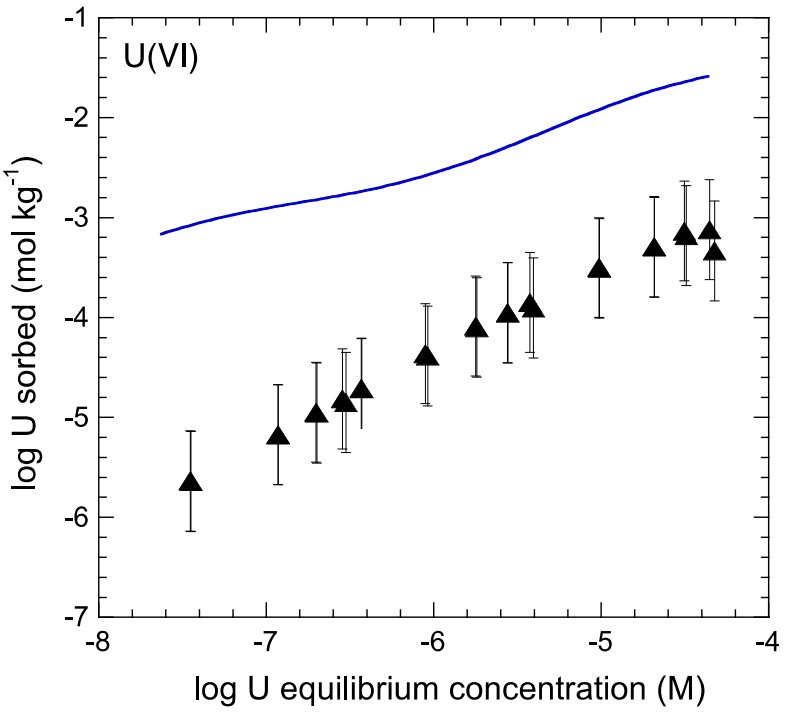


Illustration of the “bottom-up” approach

U(VI) on Boda Claystone

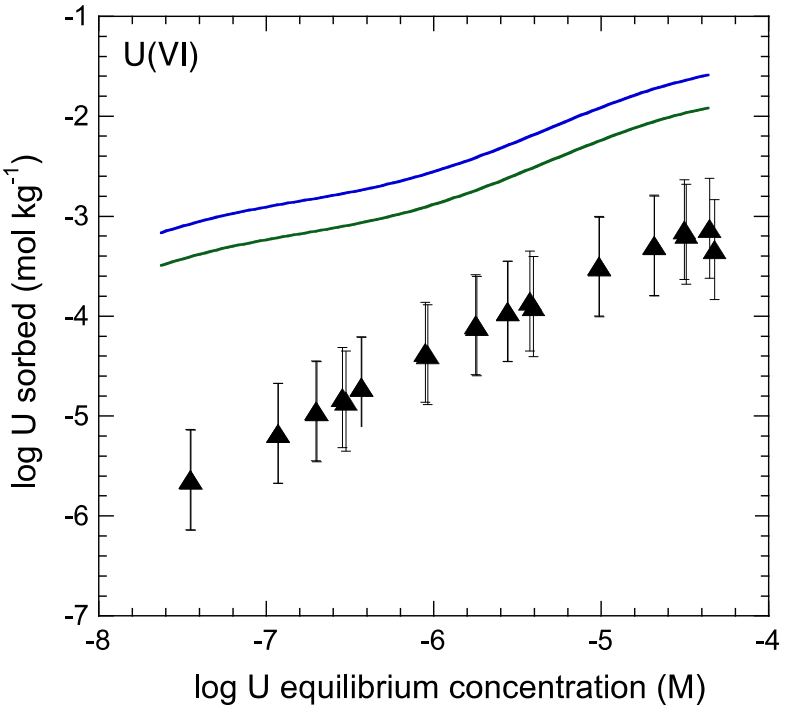


Experimental data

Illite model

Illustration of the “bottom-up” approach

U(VI) on Boda Claystone



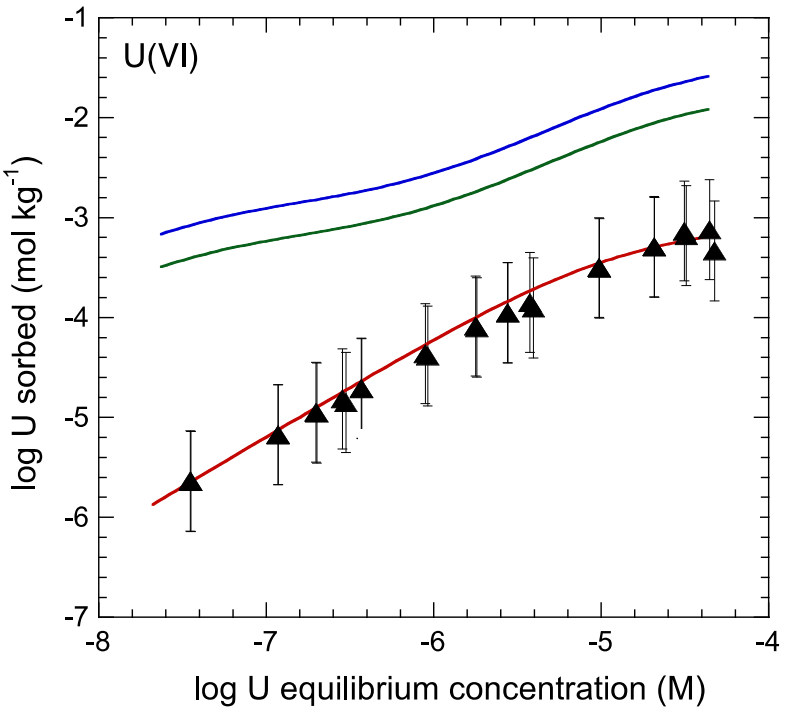
Experimental data

Illite model

scaled to the clay amount

Illustration of the “bottom-up” approach

U(VI) on Boda Claystone



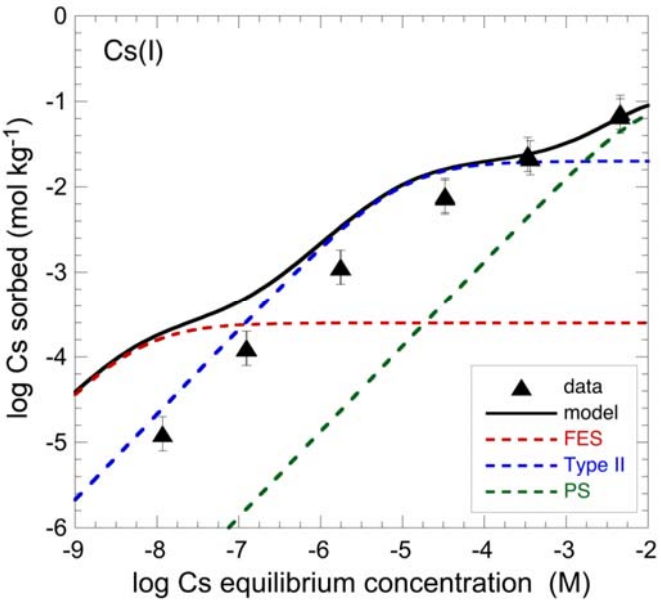
Experimental data

Illite model

scaled to the clay amount

Porewater composition

Blind predictions for Cs(I) on Boda clay

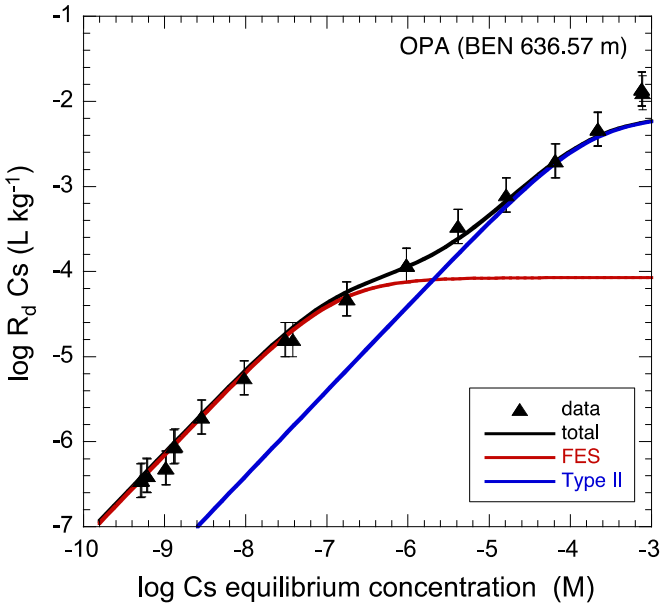


Cs(I)

- Only Type II sites and planar sites active
- The frayed edge sites may be blocked with stable Cs (slow desorption kinetics) or absent in the case of muscovite

Blind predictions for Cs(I) on OPA clay

Parameters:
17 wt.-% illite
[K] = 4.2 x 10^{-3} M
[Na] = 0.16 M



Cs(I)

- Active sites: Type II and FES, planar sites > 10^{-3} M $[Cs]_{eq}$

Same approach can be used for soils with a high clay content

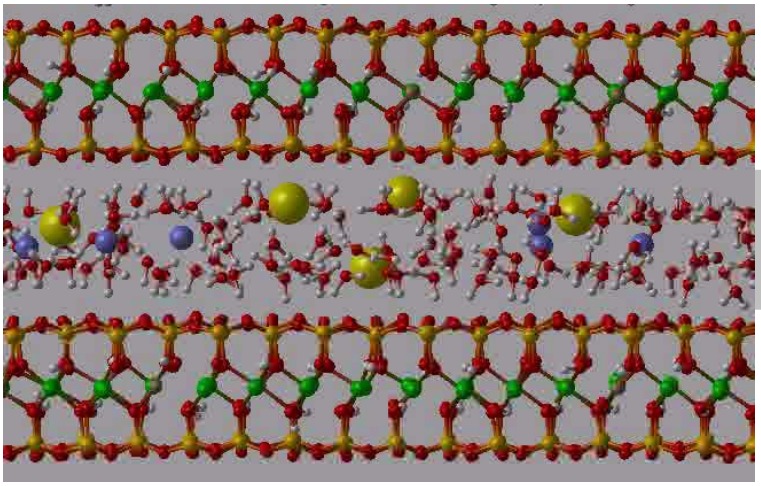
Water and cation diffusion in the clay interlayer

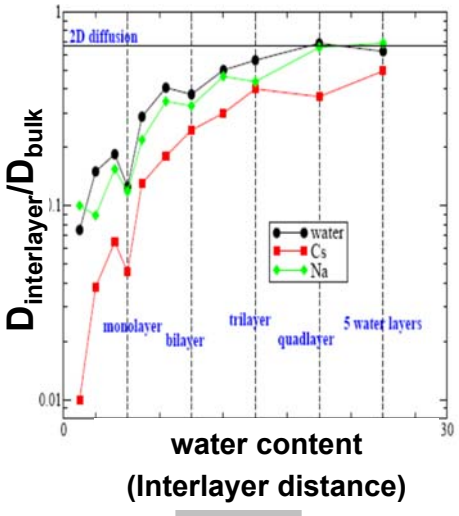
Molecular dynamics simulations:

$$M_k \frac{d^2 R_k}{dt^2} = -\frac{\partial U(R)}{\partial R_k}$$

$$\left\langle \left| \boldsymbol{R_k}(t_0 + t) - \boldsymbol{R_k}(t_0) \right|^2 \right\rangle \rightarrow 2n\mathbf{D}\ t$$

Cs-Na-Montmorillonite T=300K, P=1bar



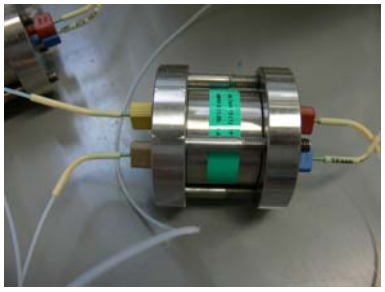


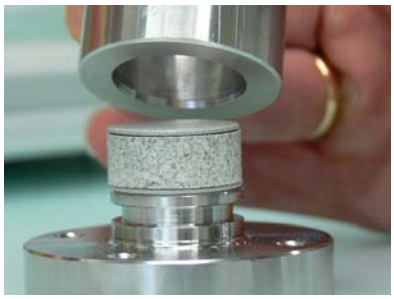
Froideval, et al., J. Nuc. Mat. 2011

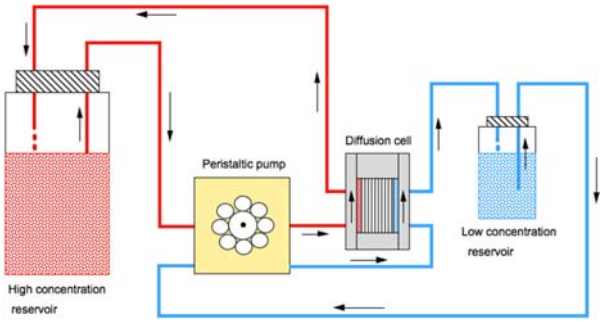
Kosakowski, et al., Clays Clay Miner. 2008

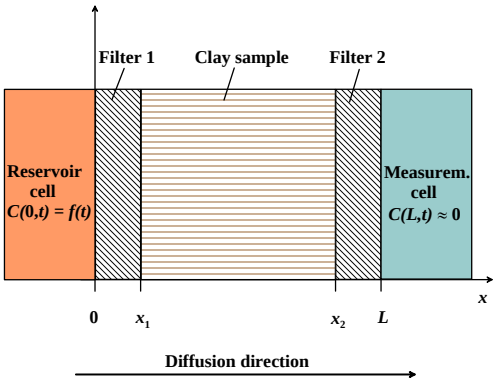
Modeling of Cs diffusion in Opalinus Clay

Experimental setup

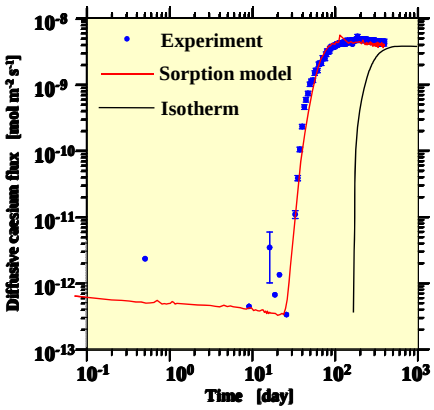








Competition aspects of ion transport in clays



$$\frac{\partial C_i}{\partial t} = \frac{D_e}{\varepsilon}\frac{\partial^2 C_i}{\partial x^2} - R_i$$

Non-linear isotherm

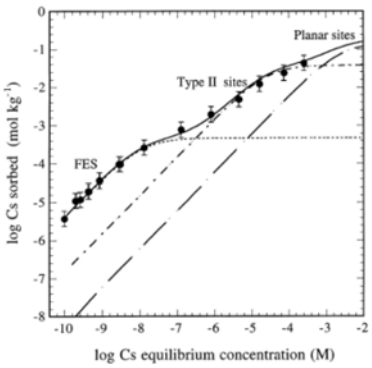
$$[Cs^{Sorbed}] = K_d(C)[Cs^{Solution}]$$

Illite sorption model

$$[Cs^{Sorbed}]_{Planar} = {}^{Cs}_{K}K_{Planar}\frac{[Cs^{Solution}]}{[K^{Solution}]}Q_{Planar}$$

$$[Cs^{Sorbed}]_{T-II} = {}^{Cs}_{K}K_{T-II}\frac{[Cs^{Solution}]}{[K^{Solution}]}Q_{T-II}$$

$$[Cs^{Sorbed}]_{FES} = {}^{Cs}_{K}K_{FES}\frac{[Cs^{Solution}]}{[K^{Solution}]}Q_{FES}$$



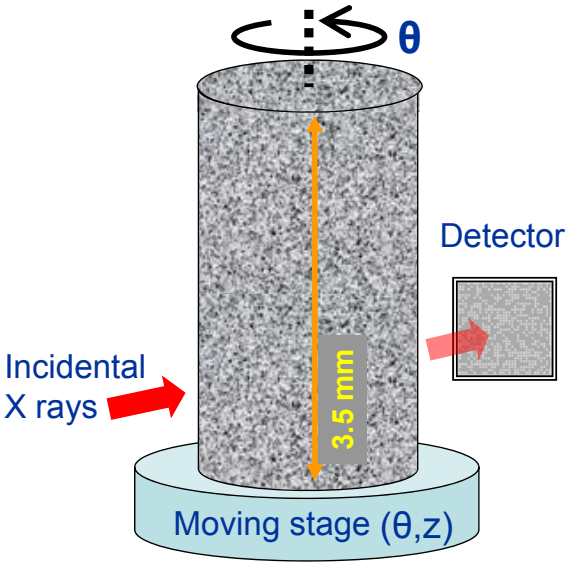
- Nonlinear sorption isotherm can not adequately explain Cs diffusion in Opalinus Clay
- Multi-species reactive transport simulations based on mechanistic sorption model describe batch sorption data and diffusion in compacted clays consistently
- Competition with K is by far the most important factor for Cs transport

Jakob. et al., Geochim. Cosmochim. Acta 2009

Mineralogical heterogeneities in Opalinus Clay

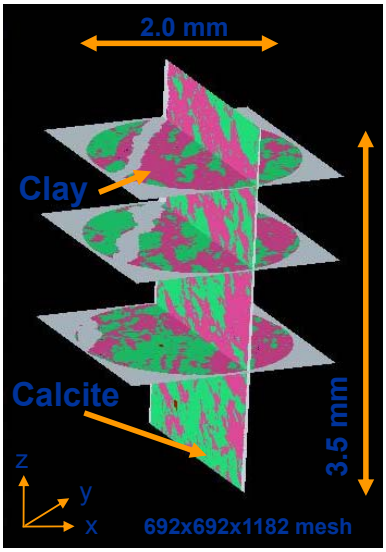
μm to mm scale

X-ray micro tomography measurement
In Opalinus Clay



TOMCAT beamline PSI
Resolution: 3x3x3 μm³

X-ray tomography measurement
In Opalinus Clay

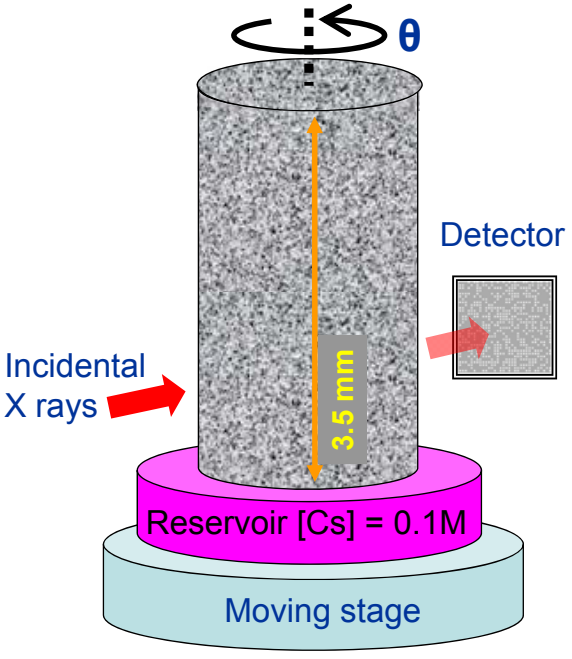


TOMCAT beamline PSI
Resolution: 3x3x3 μm³

Diaz, et al., Project Rep. 2011

Cs transport in Opalinus Clay (OPA) at μm scale

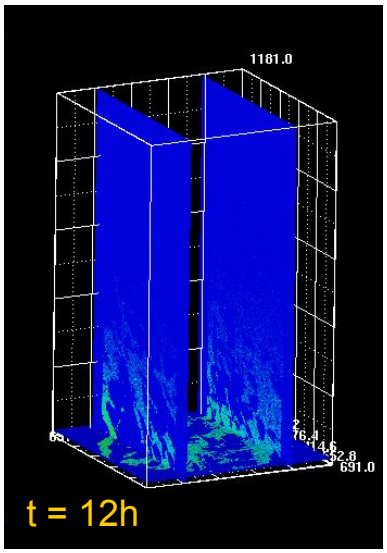
In-situ diffusion experiment
Cs-adsorption edge measurements



TOMCAT beamline PSI Resolution: 3x3x3 μm³

t = 2h, 12h, 18h, 36h

Measured
3D Cs tracer distribution



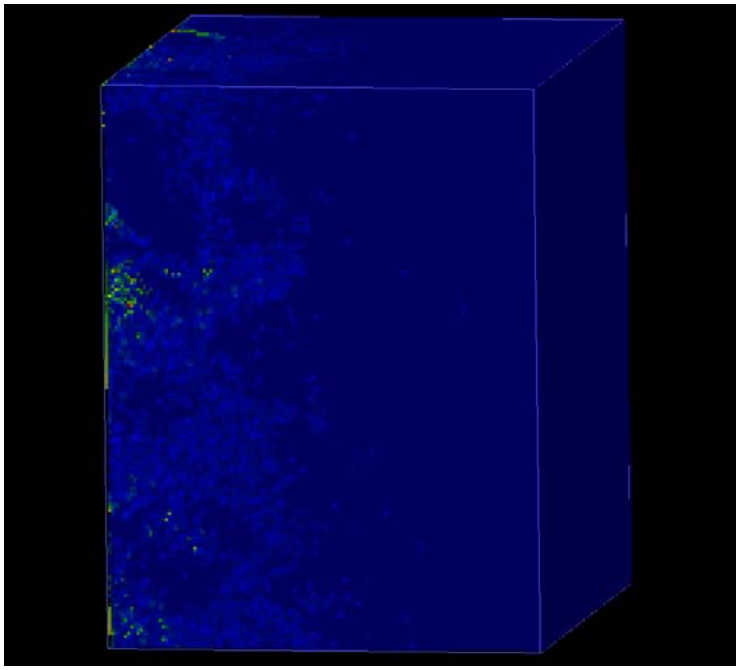
692x692x1182 mesh
Resolution: 3x3x3 μm³

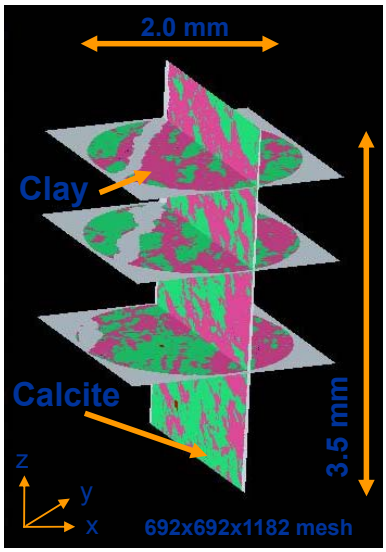
Diaz, et al., Project Rep. 2011

Cs transport in Opalinus Clay: μm => mm

Direct random walk simulation at μm resolution

692x692x1182 equidistant mesh with 3x3x3 μm^3 resolution

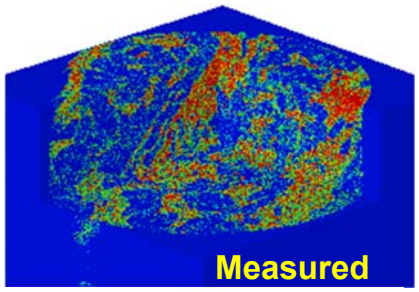


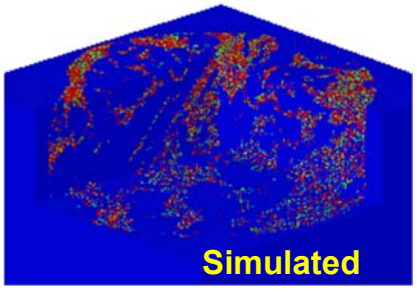


Churakov 2011

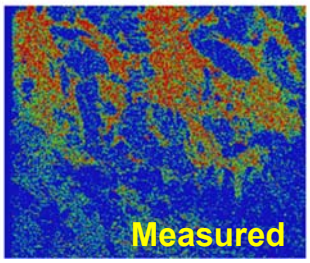
Simulated versus measured Cs concentration

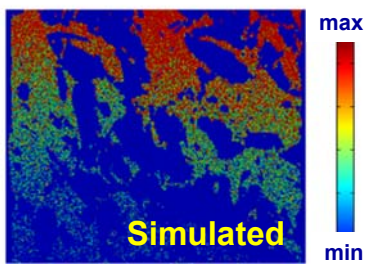
A 3D Cs distribution in OPA





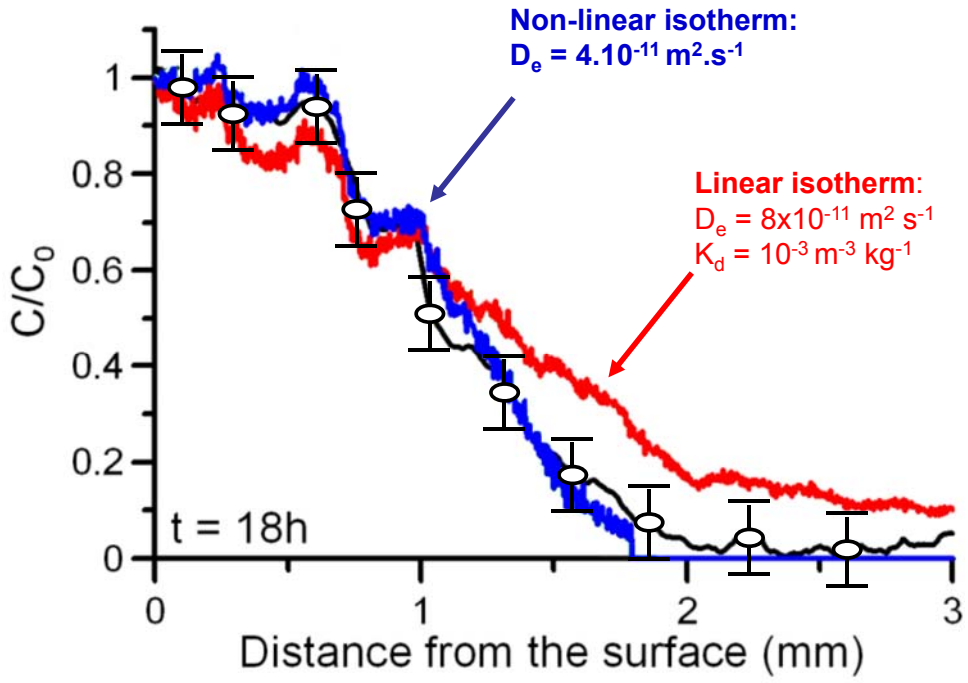
A 2D Cs distribution



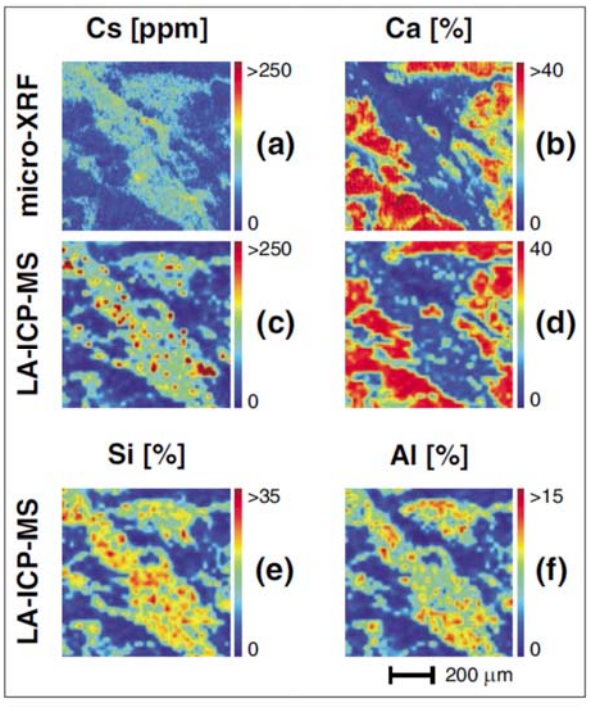


692x692x1182 mesh

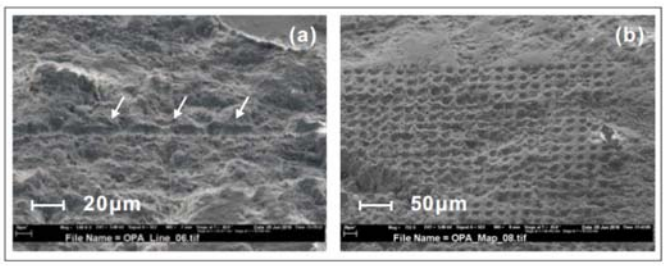
1D Cs profile: Linear and non-linear isotherms



Cs uptake by OPA

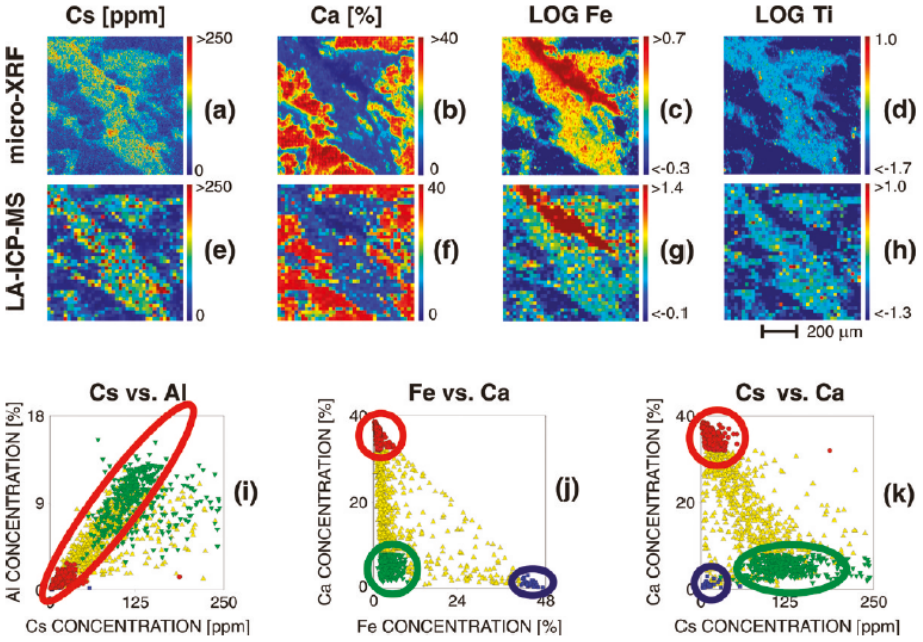


Comparison of 2D chemical images recorded by SR-microXRF (3x3 µm) and LA-ICPMS (10x10 µm)



Wang et al., Chimia 2012

Cs uptake by OPA



Wang et al., Anal. Chem. 2011

Potential role to support Fukushima challenges

Most studies concentrated on the investigation of pure mineral Phases and on potential argillaceous host rocks

	Opalinus	Boda
Mineralogy	wt. %	wt. %
Illite & Illite-Smectite mixed layer	17 & 30	--
Illite/Muscovite	--	50
Chlorite	6	--
Kaolinite	21	--
Quartz	9	8
Calcite	7	8
Dolomite/Ankerite	2	--
K-feldspar/Albite	1	17
Siderite	6	--
Pyrite	0.9	--
Hematite	--	6
Analcime	--	10

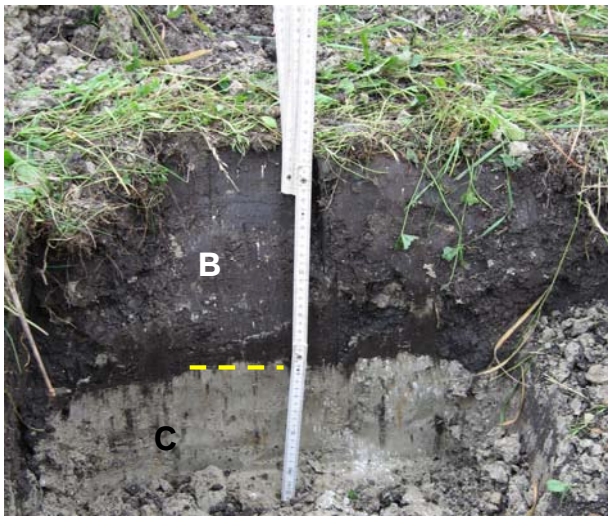
	Opalinus	Boda
Porewater		
pH	7.8	8.1
I (M)	0.23	0.02 M
Dissolved constituents (M)		
Na	$1.6 \cdot 10^{-1}$	$1.7 \cdot 10^{-2}$
K	$2.6 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$
Mg	$9.2 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
Ca	$1.2 \cdot 10^{-2}$	$3.1 \cdot 10^{-3}$
Cl	$1.6 \cdot 10^{-1}$	$2.3 \cdot 10^{-2}$
CO_3/HCO_3	$5.4 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$
SO_4	$2.4 \cdot 10^{-2}$	$6.1 \cdot 10^{-4}$
Si	$1.8 \cdot 10^{-4}$	-----

Fukushima soils are inherently more complex

Example: Zn smelter in France

Topsoil:
- Depth: 2-10 cm= **B horizon**
- **Zn: 1100 ppm**
- pH: 8
- TOC: 60 g/kg
- $CaCO_3$: 120 g/Kg
- **Clays: 20 %** (240 g/kg)
- Silt: 64% (634 g/kg)
- Sand: 13% (126 g/kg)

Subsoil :
- Depth: 30-40 cm= **C horizon**
- **Zn: 70 ppm**
- pH: 8.5
- TOC: 10 g/Kg
- $CaCO_3$: 160 g/Kg
- **Clays: 20 %** (248 g/kg)
- Silt: 65% (574 g/kg)
- Sand: 14% (178 g/kg)

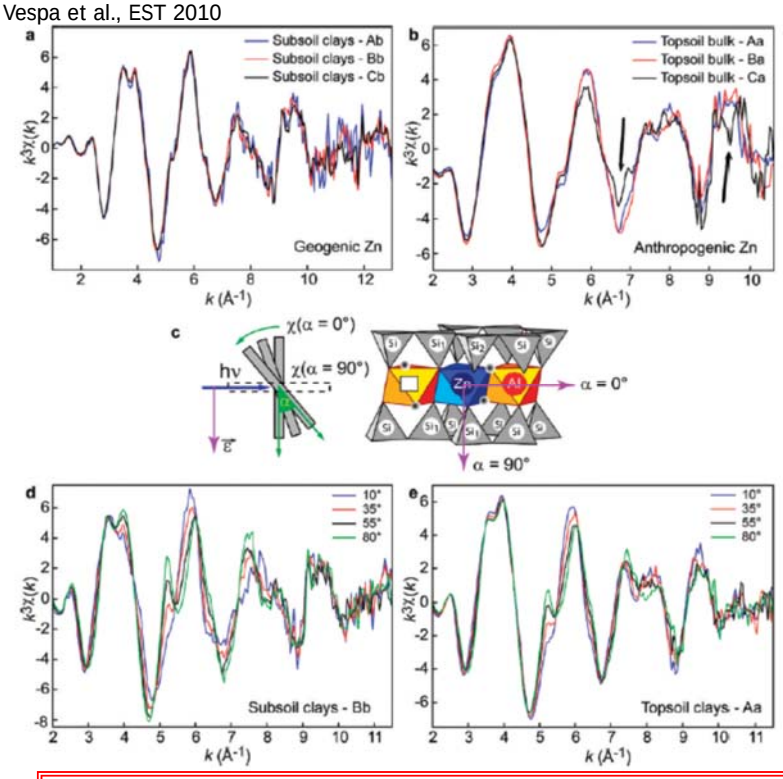


Vespa et al., ES&T 2010

Bottom-up approach should be applicable in clay-rich soils

Zn in soils: Bulk+P-EXAFS

Vespa et al., EST 2010



Bulk soil sample:
Aa: 1100 ppm
Bb: 70 ppm

P-EXAFS clay fraction:
Aa: 2250 ppm
Bb: 160 ppm

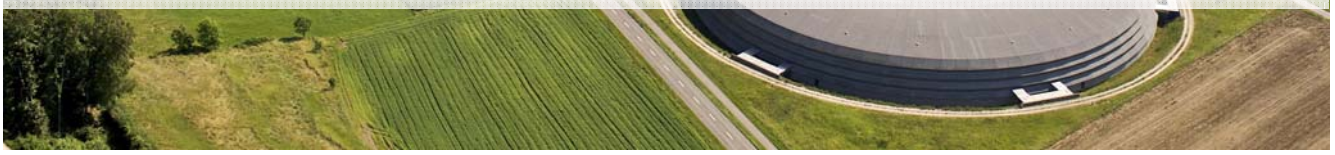
Extraction of the clay fraction and perform P-EXAFS

Conclusions

- **Advanced spectroscopic and modeling methods, complemented with wet chemistry, are powerful tools to develop remediation strategies of contaminated soils**
- **Combination of bulk-, polarized, micro-XAS/XRF/XRD is a key element to investigate complex heterogeneous systems**
- **Results can help to predict the fate of contaminants in Fukishima soils and quantify the uptake processes**
- **System understanding gives strong public credibility**

Geochemical implications:

deep understanding of uptake processes at the water/clay interface at a molecular level



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Cordially invite you to participate in the ANXAS-2014 at PSI

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Mineralogy & porewater composition

	Opalinus	Boda
Mineralogy	wt. %	wt. %
Illite & Illite-Smectite mixed layer	17 & 30	--
Illite/Muscovite	--	50
Chlorite	6	--
Kaolinite	21	--
Quartz	9	8
Calcite	7	8
Dolomite/Ankerite	2	--
K-feldspar/Albite	1	17
Siderite	6	--
Pyrite	0.9	--
Hematite	--	6
Analcime	--	10

	Opalinus	Boda
Porewater		
pH	7.8	8.1
I (M)	0.23	0.02 M
Dissolved constituents (M)		
Na	$1.6 \cdot 10^{-1}$	$1.7 \cdot 10^{-2}$
K	$2.6 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$
Mg	$9.2 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
Ca	$1.2 \cdot 10^{-2}$	$3.1 \cdot 10^{-3}$
Cl	$1.6 \cdot 10^{-1}$	$2.3 \cdot 10^{-2}$
CO_3/HCO_3	$5.4 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$
SO_4	$2.4 \cdot 10^{-2}$	$6.1 \cdot 10^{-4}$
Si	$1.8 \cdot 10^{-4}$	-----

Boda Claystone Formation, Southern Hungary	Opalinus clay, Northern Switzerland
250 Ma	180 Ma
Deposition in a shallow lacustrine environment	Deposition in shallow marine environment
monotonous, albititic, partly cross-bedded or laminated poorly bedded siltstone with conglomerate, sandstone, and dolomitic intercalations. Red and reddish brown, reflecting the dominantly oxidizing nature of the depositional environments	dark grey claystone, five sub-units can be distinguished, on the basis of slight variations in the carbonate/clay ratio
Depth ~1000 m	~ 500 m

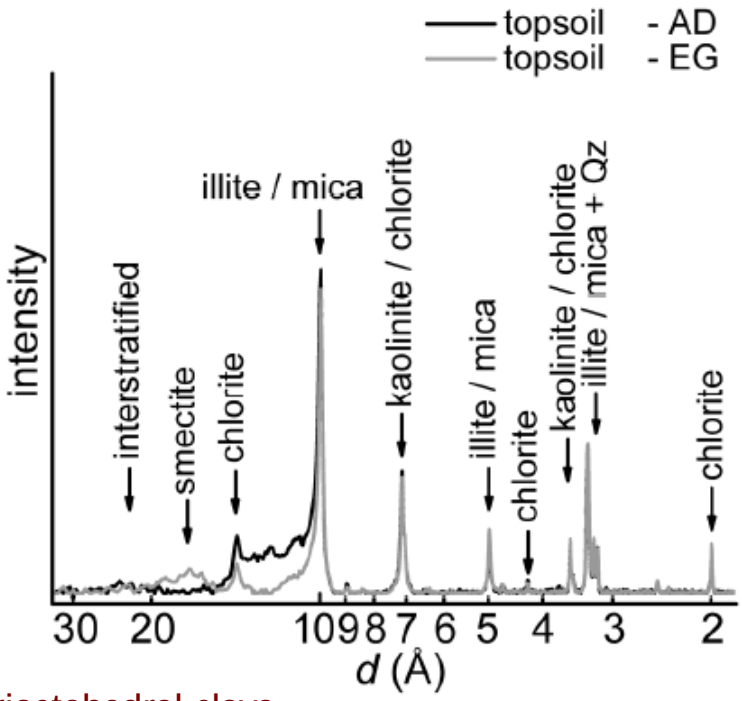
Bulk-XRD

Identification of Zn species in the matrix in the Topsoil

➡ bulk-XRD

AD: air dried

EG: ethylene glycol
→Increases Sensitivity to smectite



➡ Presence of both di- and trioctahedral clays

Vespa et al., EST 2010

Micro-XRD

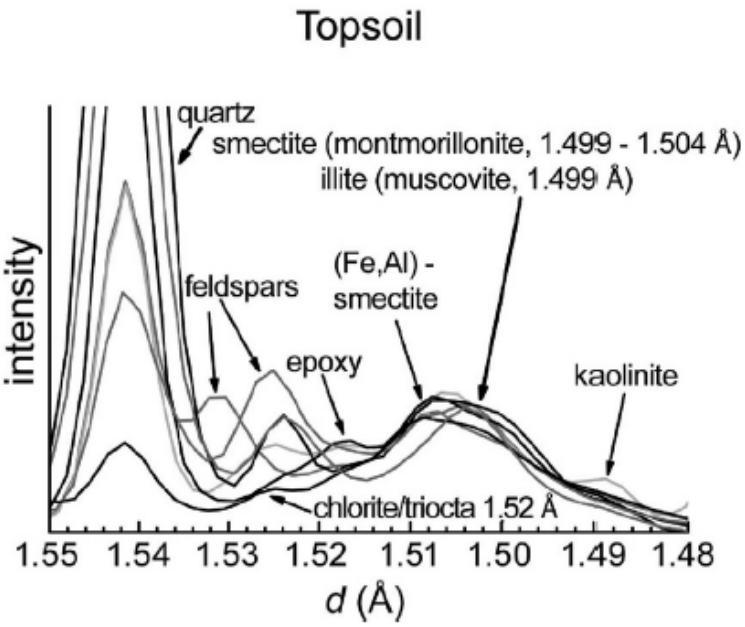
Identification of Zn species in the matrix in the Topsoil

➡ μ-XRD

060 reflection

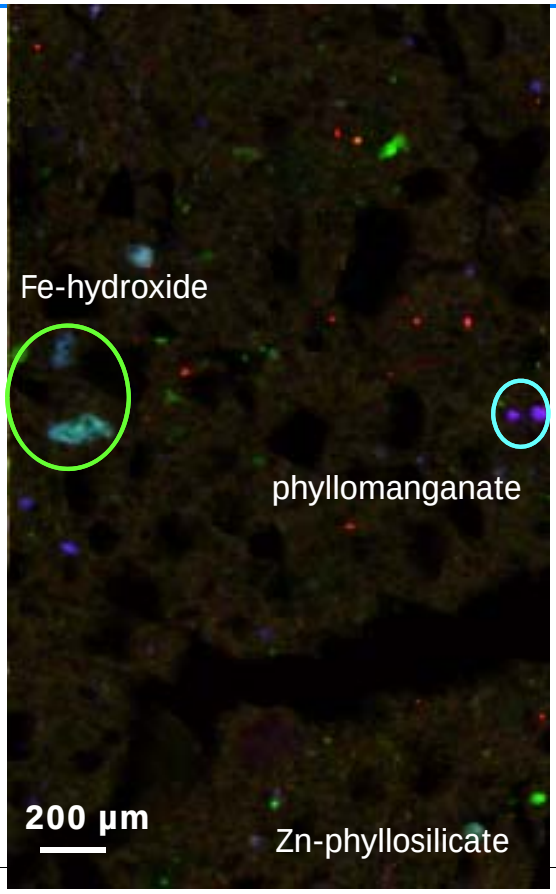
→Characteristic for clays

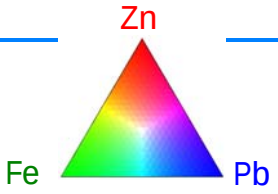
➡ Presence of Fe-Al smectite



✓ Zn incorporated in Fe-containing dioctahedral clay

Micro-XRF





- Zn immobilized in clay minerals
  - Subsoil: 60-100 ppm Zn
    - Zn-Al containing clay
    - -> natural forming dioctahedral clay
  - Topsoil: 1000-300 ppm Zn
    - Zn-Al-Fe containing clay
    - -> anthropogenic forming dioctahedral clay

  => low mobility
- Zn is associated with Pb in phyllomanganate & Fe-(hydro)xides precipitates

  => mobile in reducing conditions