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A robust and parsimonious model for caesium sorption on pure clay minerals and natural clay materials

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M.A. Cherif, A. Martin-Garin, Frédéric Gérard, Olivier Bildstein. A robust and parsimonious model for caesium sorption on pure clay minerals and natural clay materials. Goldschmidt Conference 2016, Jun 2016, Yokohama, Japan. pp.473. cea-02442325

HAL Id: cea-02442325

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Submitted on 16 Jan 2020

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*A robust and parsimonious model for
caesium sorption on pure clay minerals
and natural clay materials*

GOLDSCHMIDT
YOKOHAMA 2016
26 JUNE - 1 JULY

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Context & objective

Pure clay minerals

Development a robust and parsimonious model for Cs sorption
Comparison to available Cs sorption models

natural clay materials

Testing & Application of developed model using component additivity (CA) approach

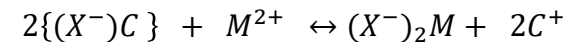


Conclusion & Perspectives

Multi-site Cation Exchange models

Clay mineral	Reference	Cs sorption model
Illite	Brouwer et al. (1983)	3-sites CE
	Bradbury and Baeyens (2000) (GCS model)	3-sites CE
	Benedicto et al. (2014)	3-sites CE
	Savoie et al. (2012)	5-sites CE
	Missana et al. (2014b)	3-sites CE
Kaolinite	Missana et al. (2014b)	2-sites CE
	Reinoso-Maset and Ly (2014)	2-sites CE

Ion exchange theory :



$${}^M_C K_c = \frac{[(X^-)_2M][C^+]^2}{[(X^-)C]^2[M^{2+}]}$$

uncertainty of $\log {}^C_C K_c \approx \pm 0.2$

- ✓ No compilation or comparison study of these models has ever been proposed.
- ✓ The validity of the models is usually limited to restricted field and specific physicochemical conditions.

*They appear to be **unsatisfactory** to predict Cs sorption a wide range of conditions in natural systems*



Is needed to develop of mechanistic and generic model, able to reproduce and predict the Cs sorption in simple and complex systems, and without recourse to change of model parameters for each condition,



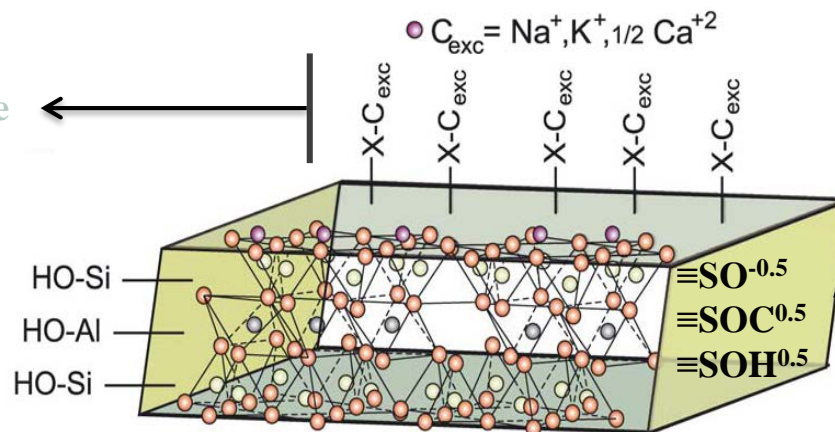
Mechanistic approach and model choice

Mineralogy parameters	Illite	Montmorillonite	Kaolinite
Site capacity of non specific sites (meq kg ⁻¹) (CEC)	190 - 225	870	20
Site density of specific sites (sites nm ⁻²)	2.7 · 10 ⁻³	3.6 · 10 ⁻⁵	1.5 · 10 ⁻⁴
Surface Specific Area (SSA) (m ² g ⁻¹)	62 - 97	800	10

Non specific sites
negative permanent charge
(high density/low affinity)



Cation Exchange



Specific sites
variable charge
(low density/high affinity)



Surface Complexation
1-pK Double Layer Model

Parsimonious and minimalist approach

Cation exchange reactions on ≡X- sites	LogK _c		
	I	M	K
XNa + Cs ⁺ ↔ XC _s + Na ⁺	2.45	1.39	2.1
XK + Cs ⁺ ↔ XC _s + K ⁺	0.95	0.8	2.1
XNH ₄ + Cs ⁺ ↔ XC _s + NH ₄ ⁺	1.38	0.8	2.1
X ₂ Ca + 2Cs ⁺ ↔ 2XC _s + Ca ²⁺	5.2	1.7	4.49
X ₂ Sr + 2Cs ⁺ ↔ 2XC _s + Sr ²⁺	5.2	2.37	4.49
X ₂ Mg + 2Cs ⁺ ↔ 2XC _s + Mg ²⁺	5.2	2.45	4.49

Surface complexation reactions on ≡SOH sites	LogK _{SOM}		
	I	M	K
SO ^{-0.5} + H ⁺ ↔ SOH ^{0.5}	3.46	3.4	5
SOH ^{0.5} + Cs ⁺ ↔ SOC _s ^{0.5} + H ⁺	5.2	4.3	3
SOH ^{0.5} + Na ⁺ ↔ SONa ^{0.5} + H ⁺	-1.8	-1.3	-3.6
SOH ^{0.5} + K ⁺ ↔ SOK ^{0.5} + H ⁺	0.6	0.1	-1.75
SOH ^{0.5} + NH ₄ ⁺ ↔ SONH ₄ ^{0.5} + H ⁺	1.1	0.1	-1.75
SOH ^{0.5} + Ca ²⁺ ↔ SOCa ^{1.5} + H ⁺	-5	-1.4	-5.9

Values determined by fitting experimental data (this study)

Revised values from the literature

Hurel et al. (2003) / Gutierrez and Fuentes (1996) for Cs

Bradbury and Baeyens (1997, 2005) / Tournassat et al. (2013) for Ni, Zn and Mn

Benedicto et al. (2014) for Ga

Reich et al. (2010) for Pb

Gu and Evans (2007, 2008) for Cd, Cu, Ni, Pb and Zn....

Existing experimental data for pure clay minerals and models comparison

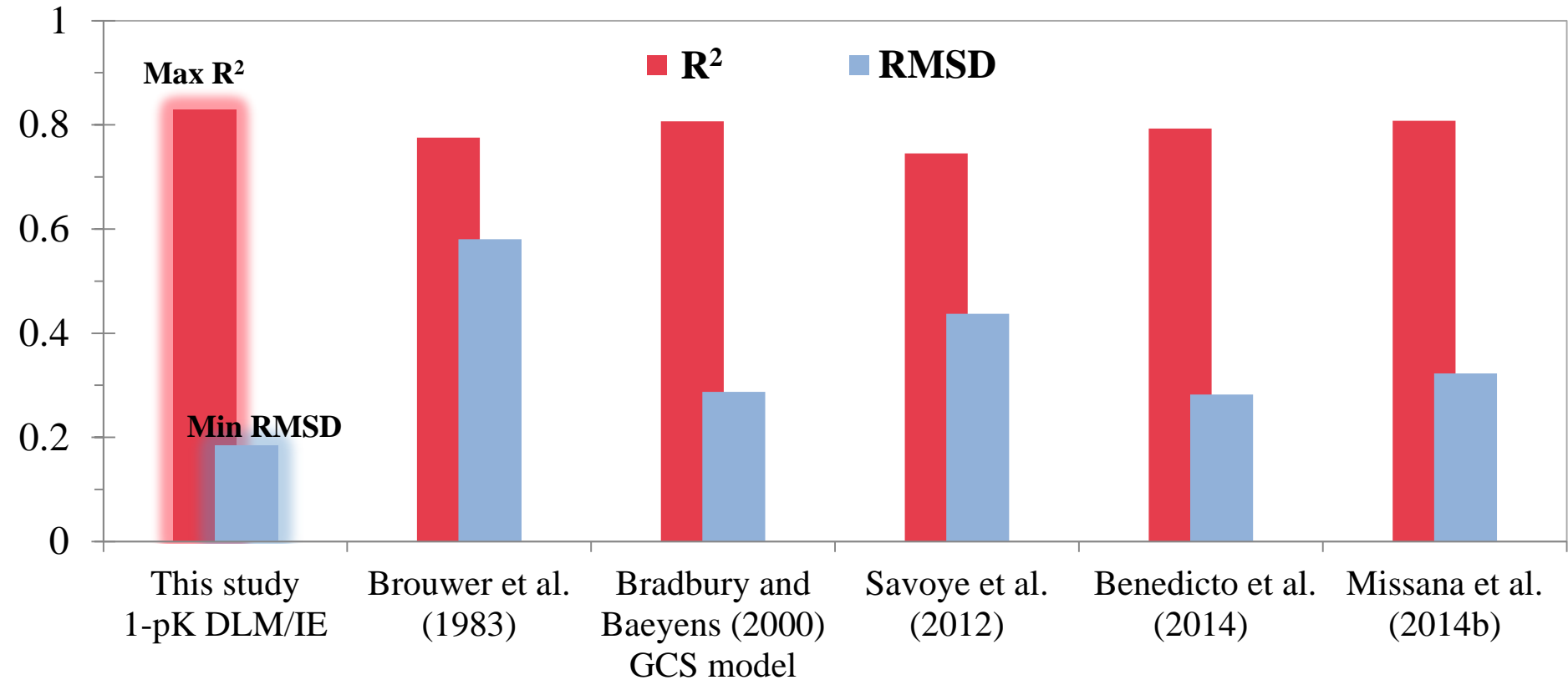
(n = 321 observations)

Clay minerals	Reference	Major cations	I (M)	pH	[Cs ⁺] _{tot} (M)	Model
Illite	Benedicto et al. (2014)	Na ⁺ / Ca ²⁺ / K ⁺	0.01	7	10 ⁻⁹ - 10 ⁻⁴	3-sites CE
	Savoie et al. (2012)	Na ⁺	0.1	6.8	8·10 ⁻⁹ - 10 ⁻⁴	5-sites CE
	Bradbury and Baeyens (2000)	Na ⁺ / K ⁺	0.01-1	2-10	10 ⁻⁹	3-sites CE (GCS model)
	Missana et al. (2014b)	Na ⁺ / Ca ²⁺ / K ⁺ / NH ₄ ⁺	0.1	7	10 ⁻⁹ - 2·10 ⁻⁴	3-sites CE
	Brouwer et al. (1983)	K ⁺	0.002/0.02	7	2·10 ⁻⁹ - 4·10 ⁻⁴	3-sites CE
Montmorillonite	Staunton and Roubaud (1997)	Na ⁺ / Ca ²⁺ / K ⁺	0.01	7	10 ⁻⁹ - 5·10 ⁻⁴	---
	Gorgeon (1994)	Cs ⁺	0.02	1-12	0.02	---
Kaolinite	Missana et al. (2014b)	Na ⁺ / Ca ²⁺ / K ⁺ / NH ₄ ⁺	0.1/0.2	7	6·10 ⁻¹⁰ - 10 ⁻³	2-sites CE
	Gorgeon (1994)	Na ⁺ / Cs ⁺	1 / 0.01	1-12	10 ⁻⁸ / 0.01	----

Calibration, simulation results and confrontations

Illite

n = 201 observations

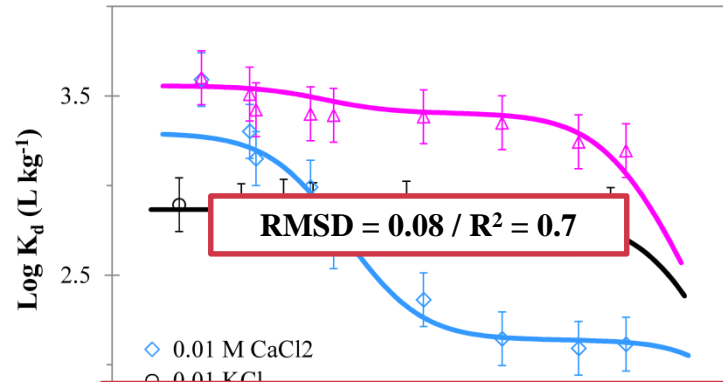


RMSD : Root Mean Square Deviation ; R^2 : Determination coefficient

Calibration, simulation results and confrontations

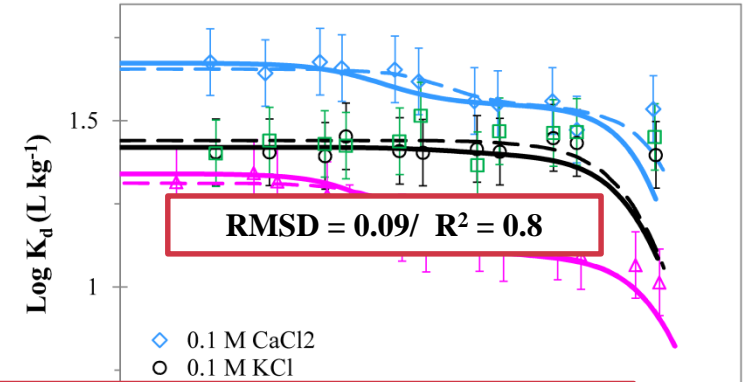
Montmorillonite

a) Sorption isotherms



Kaolinite

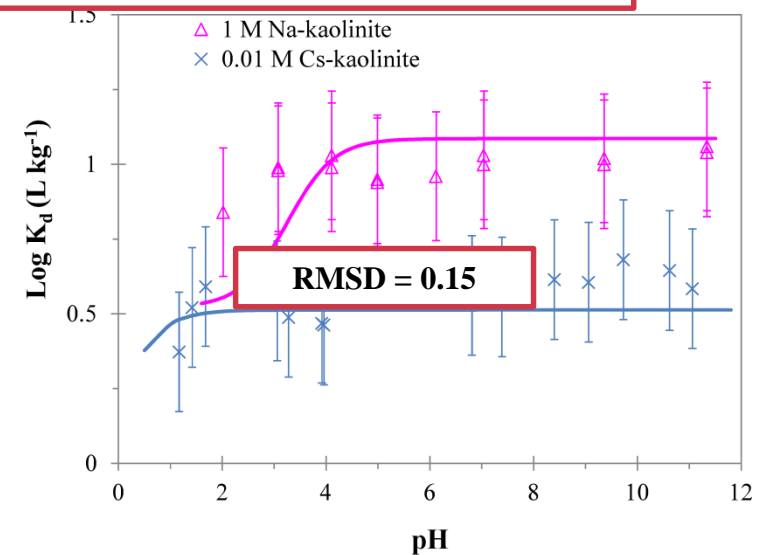
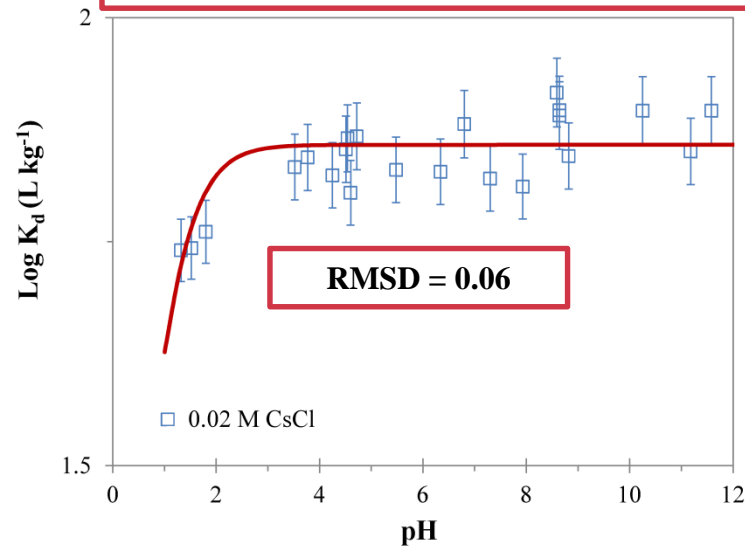
a) Sorption isotherms



Calibration : OK

- ✓ **Generic model** : very wide range of physicochemical conditions
- ✓ **Most efficient model** : accurate (RMSD<0.15) & robust ($R^2=0.82$)

b) Sorpt



Existing experimental data for natural clay materials

(n = 560 observations)

1. One clay mineral : Testing

Clay materials	Reference	Present clay minerals	Major cations	I (M)	pH	[Cs ⁺] _{tot} (M)
Hanford sediment	Zachara et al. (2002)	2.7% I	Simple conditions (Na ⁺ / Ca ²⁺ / K ⁺)	0.005 - 5	7	10 ⁻⁹ - 9·10 ⁻²
Boda Clay	Fernandes et al. (2015) (GCS model)	50% I	Natural porewater	0.033	8	10 ⁻⁷ - 10 ⁻²
MX-80 bentonite	Bradbury and Baeyens (2011)	75-84 % M	Natural porewater	0.7	7.64	6·10 ⁻⁸ - 3·10 ⁻³
	Montavon et al. (2006)			0.037	7.8	4·10 ⁻⁹ - 8·10 ⁻²

2. Mixed-clay minerals : Application

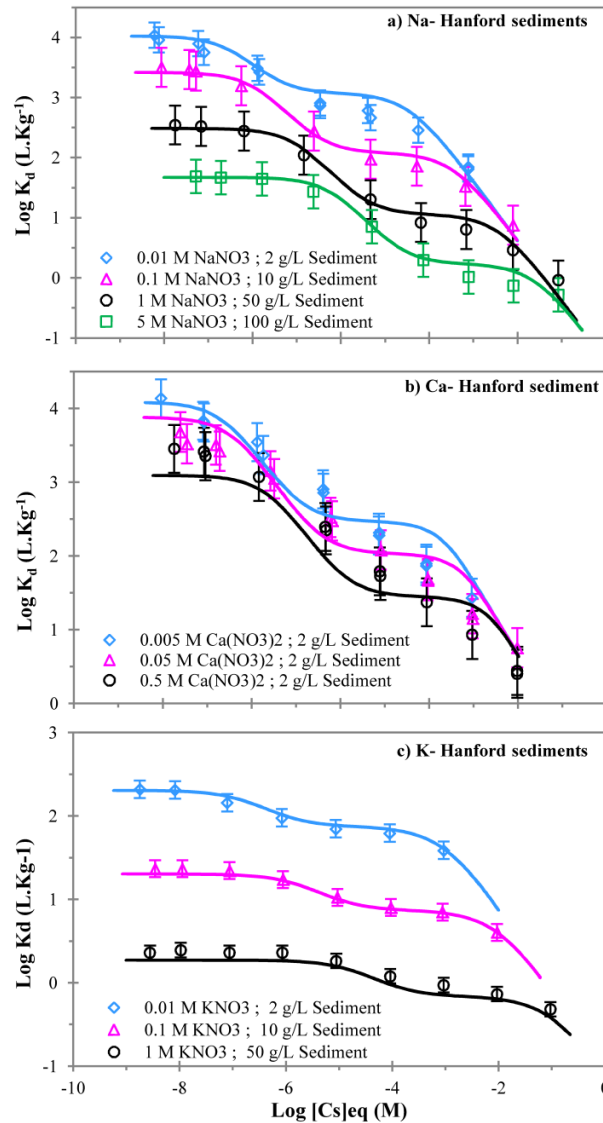
FEDEX bentonite	Missana et al. (2014a)	93% I/M with 15-10 % I	Simple conditions	0.001-0.3	7	10 ⁻⁹ - 10 ⁻²
Callovo–Oxfordian	Chen et al. (2014)	I + M + (I/M) variable	Natural porewater (Na ⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺)	0.1	7.2	5·10 ⁻⁹ - 10 ⁻⁴
	Savoie et al. (2012)			0.1	7.3	2·10 ⁻⁵ - 6·10 ⁻²
San Juan clay	Missana et al. (2014b)	30-50% I + 5-20% M + 10-15% K		0.054 / 0.46	9.4	2·10 ⁻⁹ - 10 ⁻²
Opalinus Clay	Fernandes et al. (2015) (GCS model)	17% I + 30% I/M + 21% K		0.23	7.8	10 ⁻⁸ - 10 ⁻²
Boom clay	Maes et al. (2008) (GCS model)	10-45% I + 10-30% I/M + 5-20% K		0.016	8.5	10 ⁻⁹ - 10 ⁻²

I : Illite ; M : Montmorillonite ; I/M : Illite - Montmorillonite mixed layers ; K : Kaolinite

Testing of 1-pK DLM / EI for natural clay materials : one clay mineral

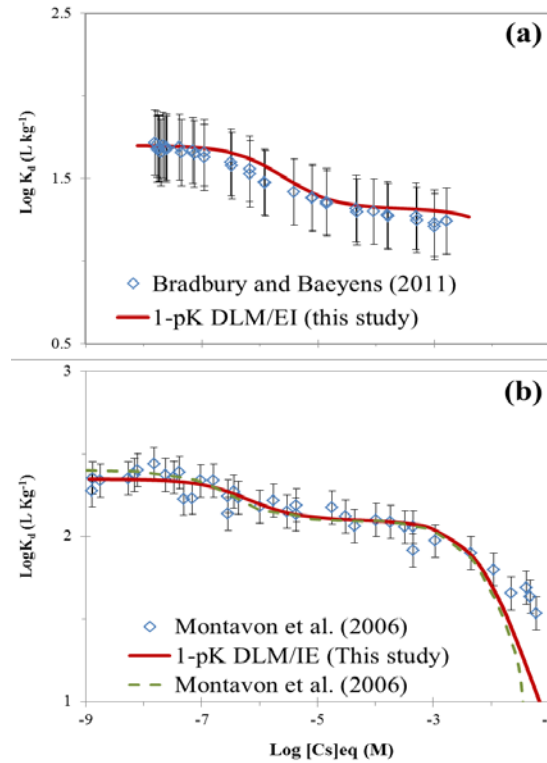
Hanford sediments

2.7% I



MX-80 bentonite

≈ 84% M

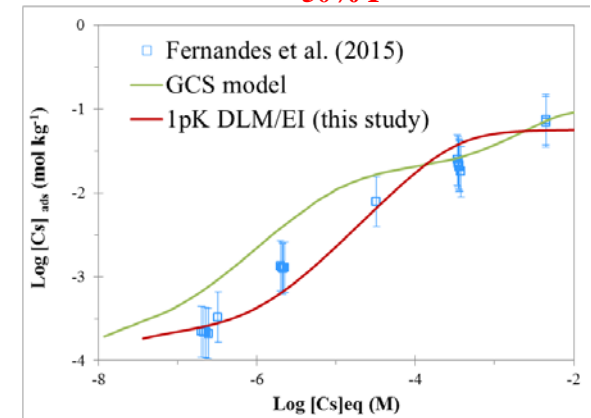


RMSD = 0.12
R² = 0.92

RMSD = 0.21
R² = 0.88

Boda clay

50% I



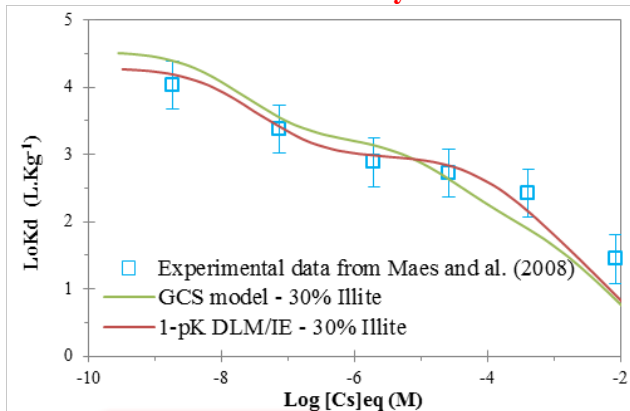
RMSD = 0.25
R² = 0.80

RMSD = 0.64
R² = 0.98

Application of 1-pK DLM / EI for natural clay materials using CA approach

Boom clay

Consideration of only 30% I

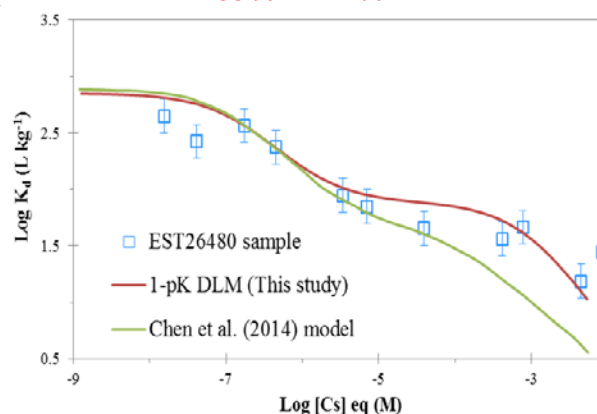


RMSD = 0.35
R² = 0.98

RMSD = 0.51
R² = 0.96

Callovo–Oxfordian sample 1

33% I + 14% M

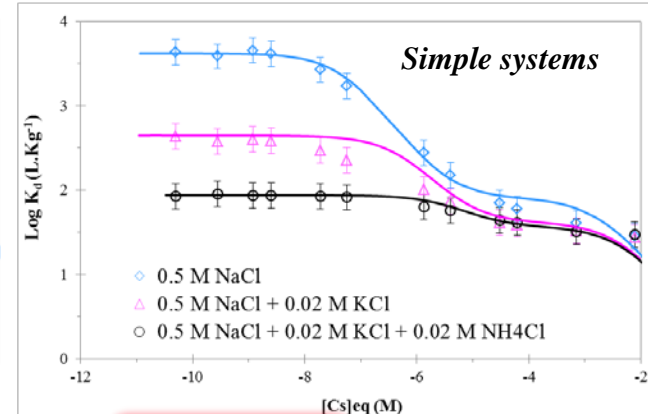


RMSD = 0.24
R² = 0.88

RMSD = 0.40
R² = 0.92

San Juan clay

40% I + 10% M + 12% K

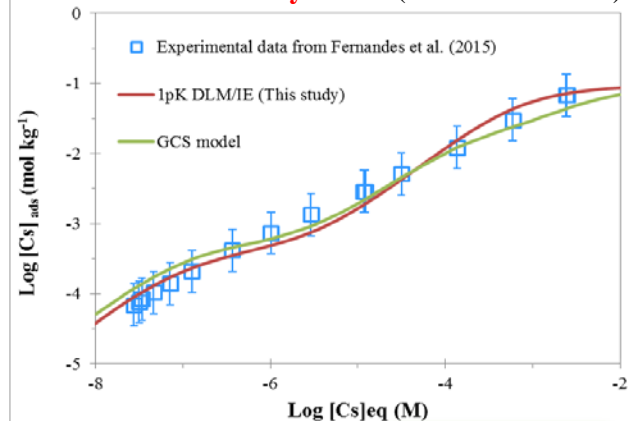


RMSD = 0.12
R² = 0.98

RMSD = 0.22
R² = 0.93

Opalinus clay

Consideration of only 47% I (17% I + 30% I/M)

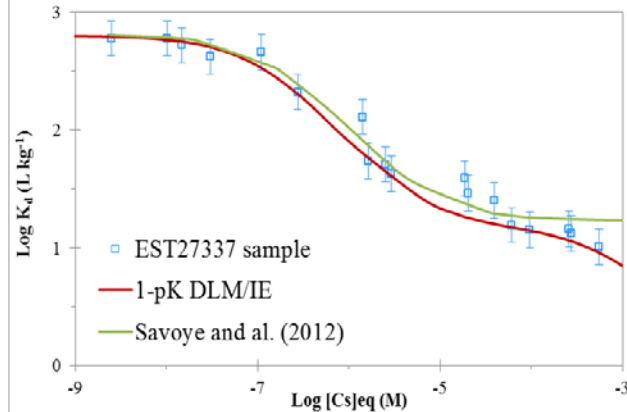


RMSD = 0.25
R² = 0.99

RMSD = 0.23
R² = 0.99

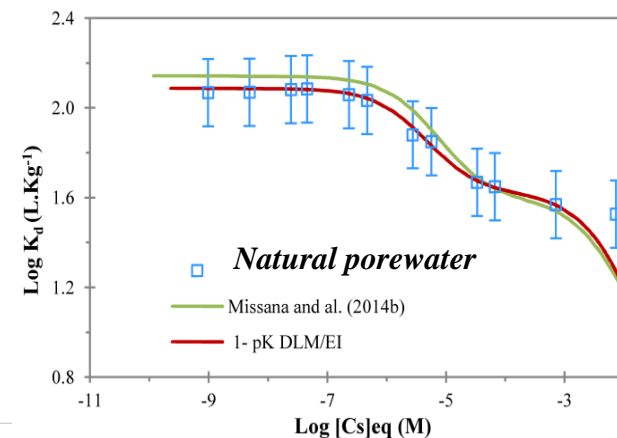
Callovo–Oxfordian sample 2

49% I + 15% M



RMSD = 0.22
R² = 0.99

RMSD = 0.22
R² = 0.89

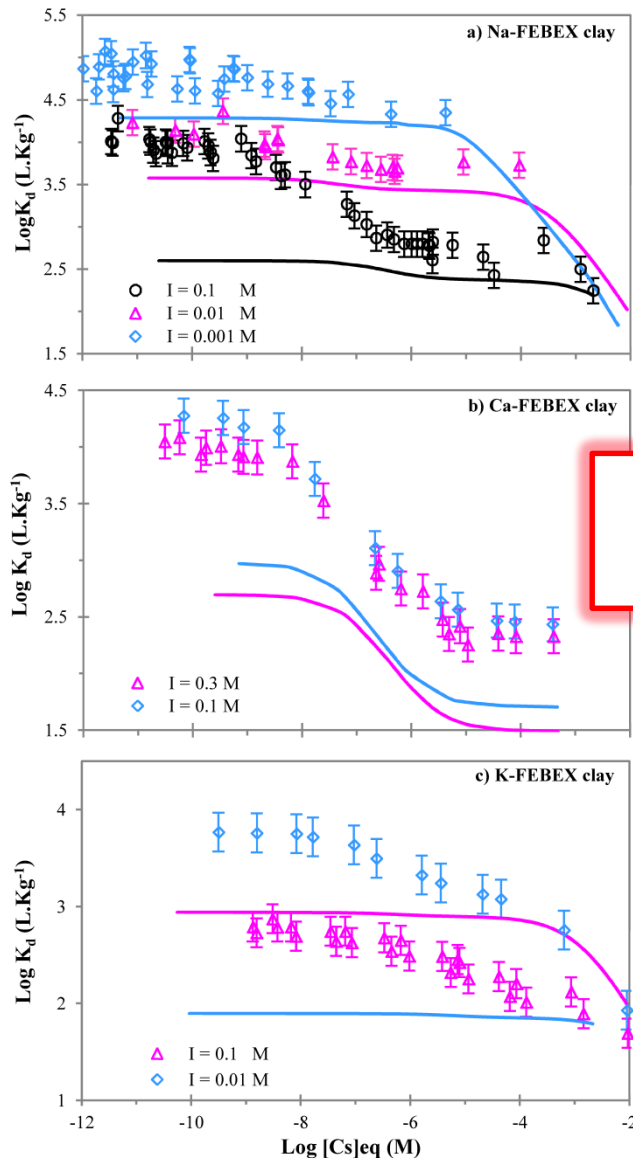


RMSD = 0.10
R² = 0.99

RMSD = 0.11
R² = 0.99

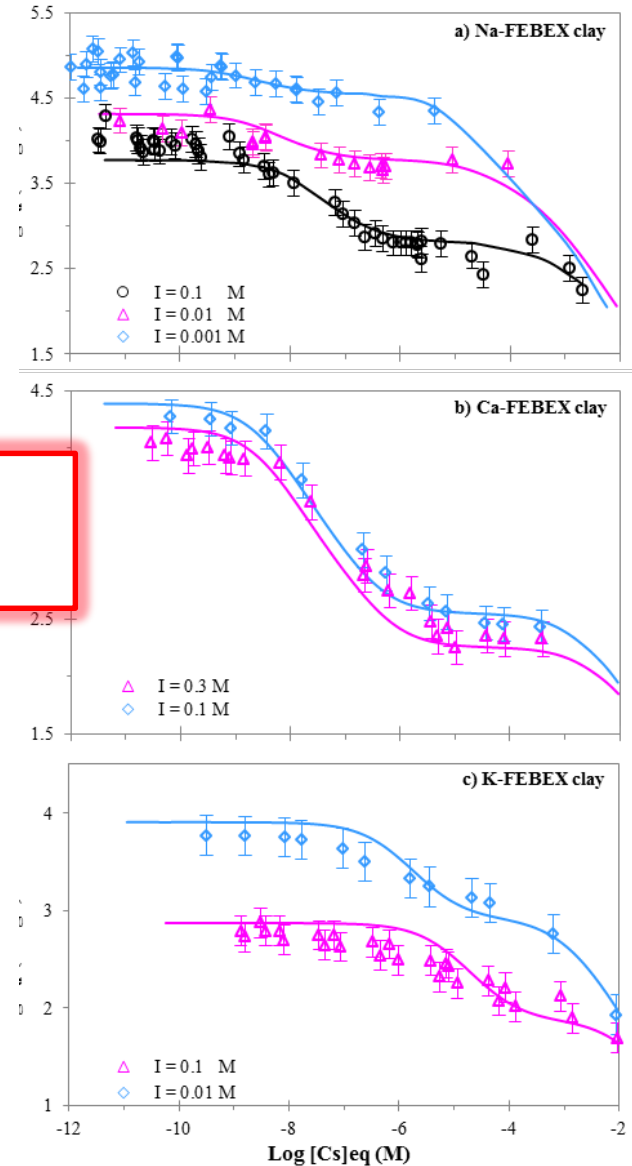
Application on FEBEX Bentonite 93% clay minerals: M with 10-15% illite layers (interstratified)

93% M - 0% illite



78% M + 15% I

RMSD = 0.18
R² = 0.87
n = 560



Development of robust and parsimonious model using minimalist and generic approach.

The result shows that our model successfully reproduces most of available experimental data both qualitatively and quantitatively.

The model account for varying levels of Cs interactions with pure and natural clay substrates, without making any prior adjustment of parameters.



Global
model

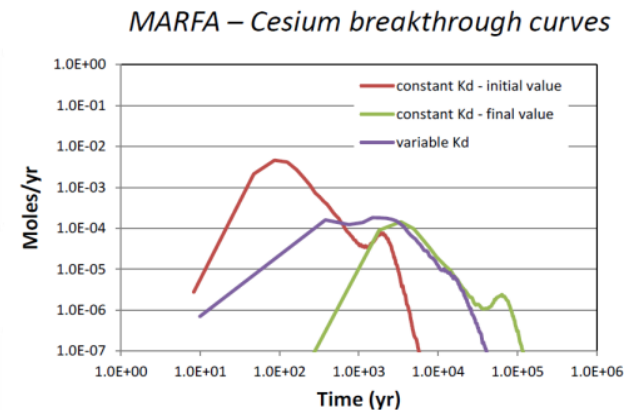
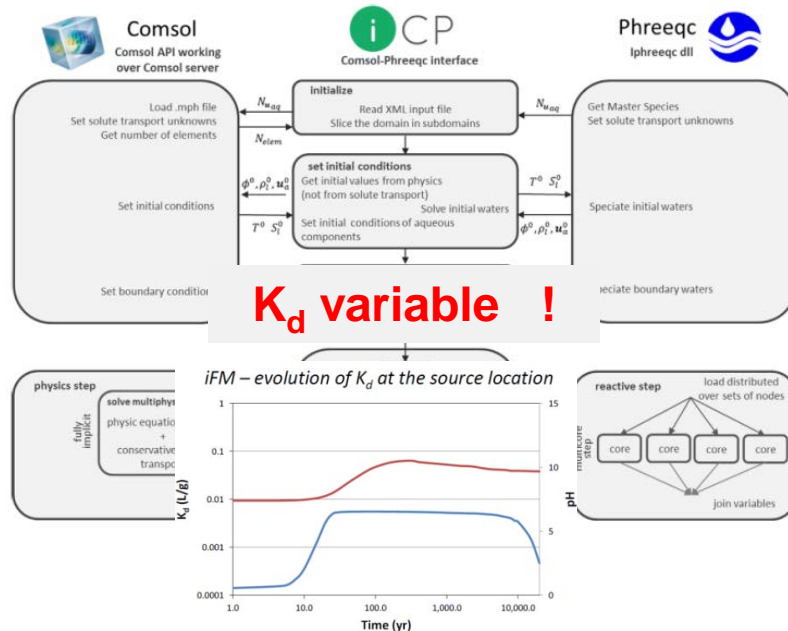
Coupling
interface

Mechanistic
model

Large number of
variable

≠

K_d constant !!



***THANK YOU FOR
YOUR ATTENTION***

GOLDSCHMIDT
YOKOHAMA 2016
26 JUNE - 1 JULY