



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

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

GOLDSCHMIDT

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26 JUNE - 1 JULY

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Pure clay
minerals

natural clay
materials

Context & objective

Development a robust and parsimonious model for Cs sorption

Comparison to available Cs sorption models

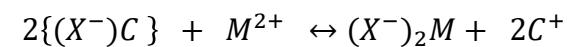
Testing & Application of developed model using component additivity (CA) approach

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
	Savoye 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 :



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

uncertainty of $\log \frac{Cs}{C} K_c \approx \pm 0.2$

- ✓ 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,

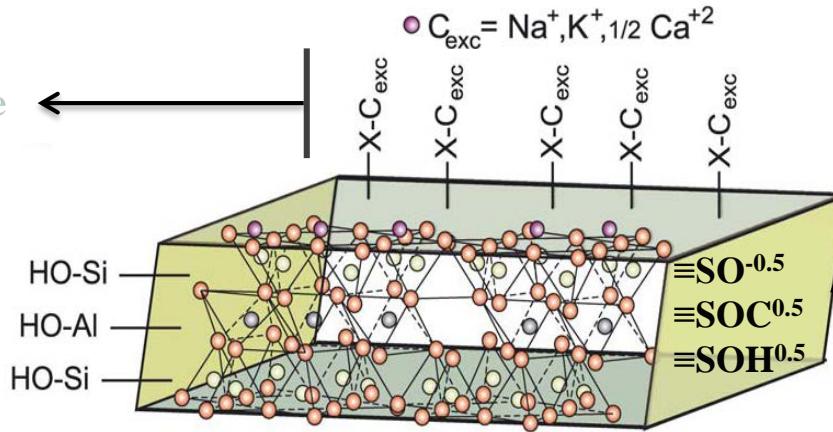
Mechanistic approach and model choice

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 ⁺	↔	XCs	+	Na ⁺	2.45
XK	+ Cs ⁺	↔	XCs	+	K ⁺	0.95
XNH ₄	+ Cs ⁺	↔	XCs	+	NH ₄ ⁺	1.38
X ₂ Ca	+ 2Cs ⁺	↔	2XCs	+	Ca ²⁺	5.2
X ₂ Sr	+ 2Cs ⁺	↔	2XCs	+	Sr ²⁺	5.2
X ₂ Mg	+ 2Cs ⁺	↔	2XCs	+	Mg ²⁺	5.2

Surface complexation reactions on ≡SOH sites				LogK _{SOM}		
		I	M	K		
SO ^{-0.5}	+ H ⁺	↔	SOH ^{0.5}		3.46	3.4
SOH ^{0.5}	+ Cs ⁺	↔	SOCs ^{0.5}	+	H ⁺	5.2
SOH ^{0.5}	+ Na ⁺	↔	SONa ^{0.5}	+	H ⁺	-1.8
SOH ^{0.5}	+ K ⁺	↔	SOK ^{0.5}	+	H ⁺	0.6
SOH ^{0.5}	+ NH ₄ ⁺	↔	SONH ₄ ^{0.5}	+	H ⁺	1.1
SOH ^{0.5}	+ Ca ²⁺	↔	SOCa ^{1.5}	+	H ⁺	-5

Values determined by fitting experimental data (this study)

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

Benedicto et al. (2014) for Ga

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

Reich et al. (2010) for Pb

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

Revised values from the literature

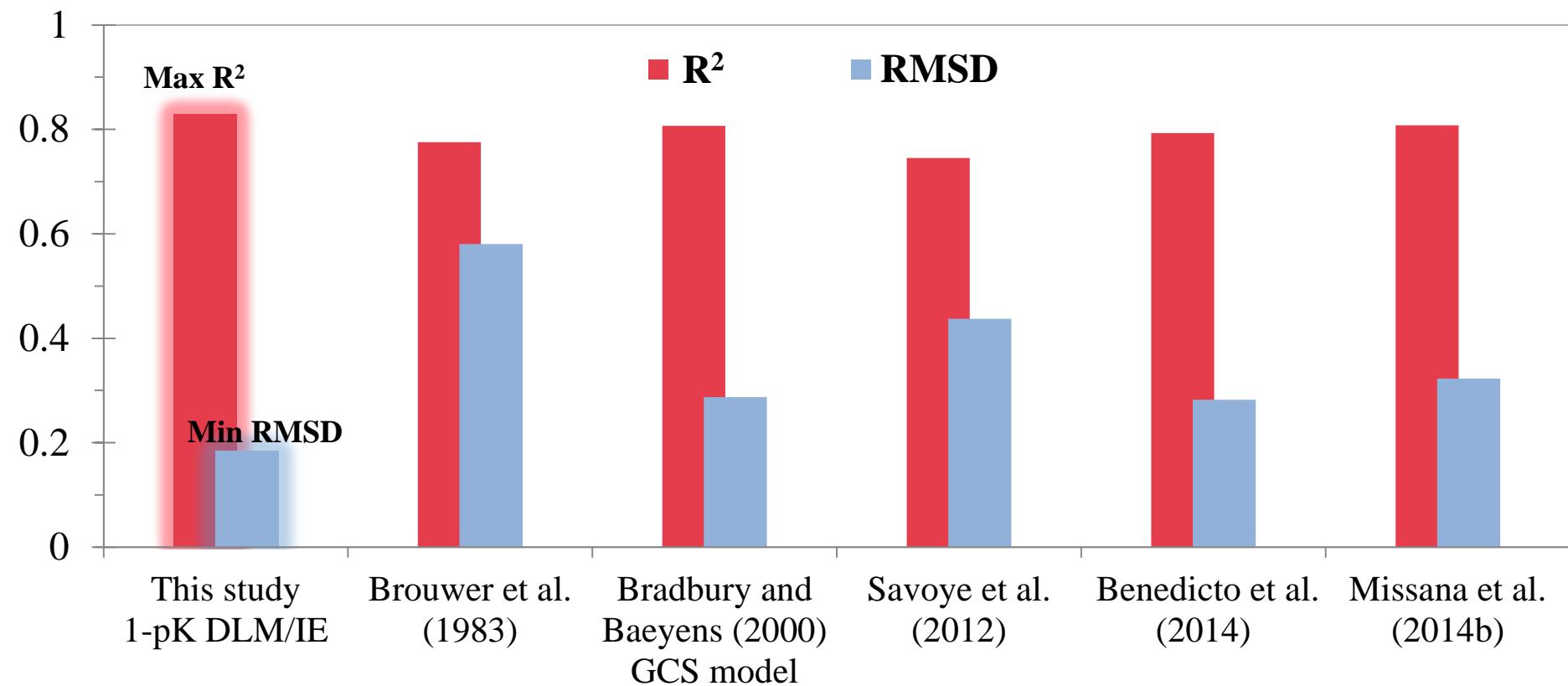
Existing experimental data for pure clay minerals and models comparison

(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
	Savoye 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
Montmorillonite	Brouwer et al. (1983)	K ⁺	0.002/0.02	7	2·10 ⁻⁹ - 4·10 ⁻⁴	3-sites CE
	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

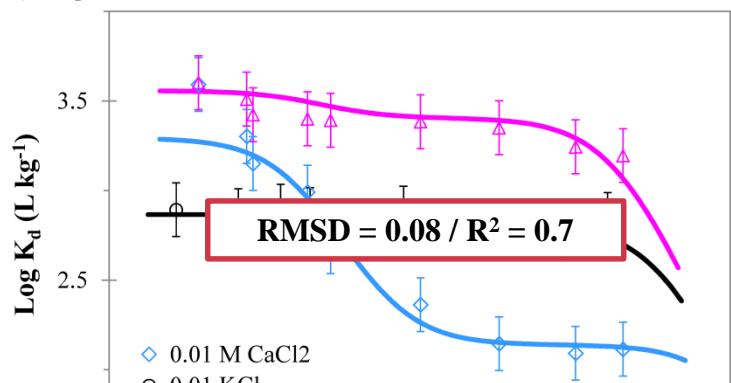
Illite

n = 201 observationsRMSD : Rout Mean Square Deviation ; R^2 : Determination coefficient

Calibration, simulation results and confrontations

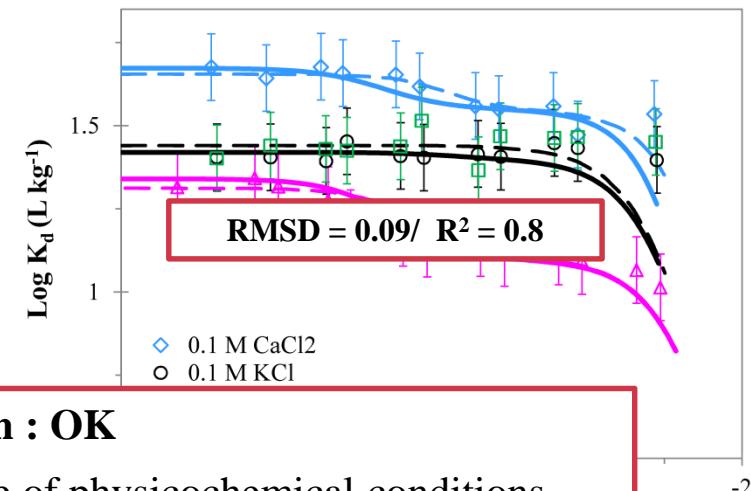
Montmorillonite

a) Sorption isotherms



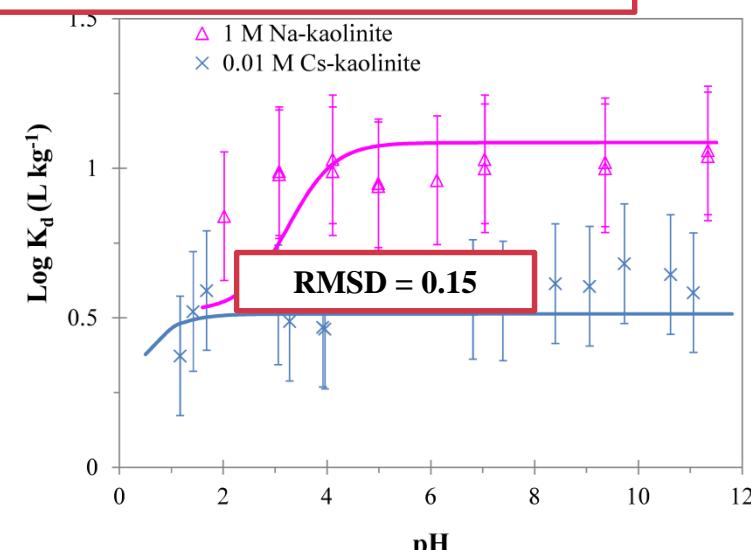
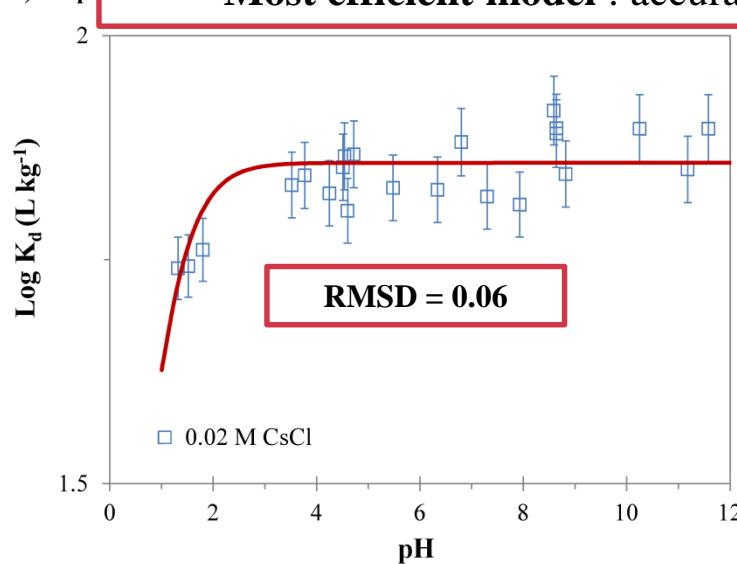
Kaolinite

a) Sorption isotherms



Calibration : OK

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

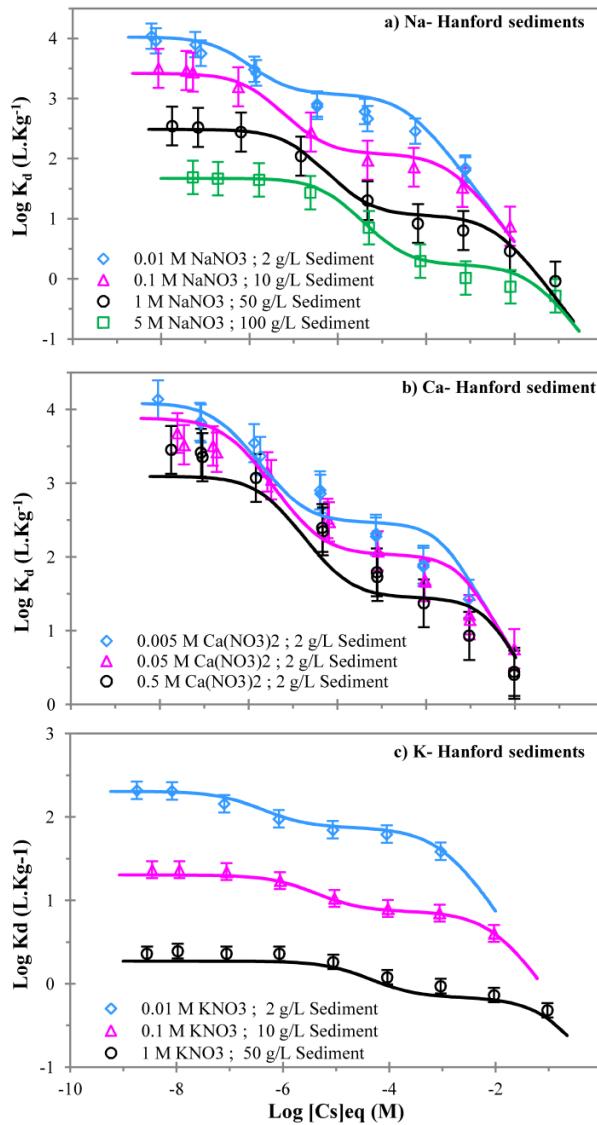
FEBEX bentonite	Missana et al. (2014a)	93% I/M with 15-10 % I	Simple conditions	0.001-0.3	7	10⁻⁹ - 10⁻²
Callovo-Oxfordian	Chen et al. (2014)	I + M + (I/M) variable	Natural porewater (Na ⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺)	0.1	7.2	5·10⁻⁹ - 10⁻⁴
	Savoye et al. (2012)			0.1	7.3	2·10⁻⁵ - 6·10⁻²
San Juan clay	Missana 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

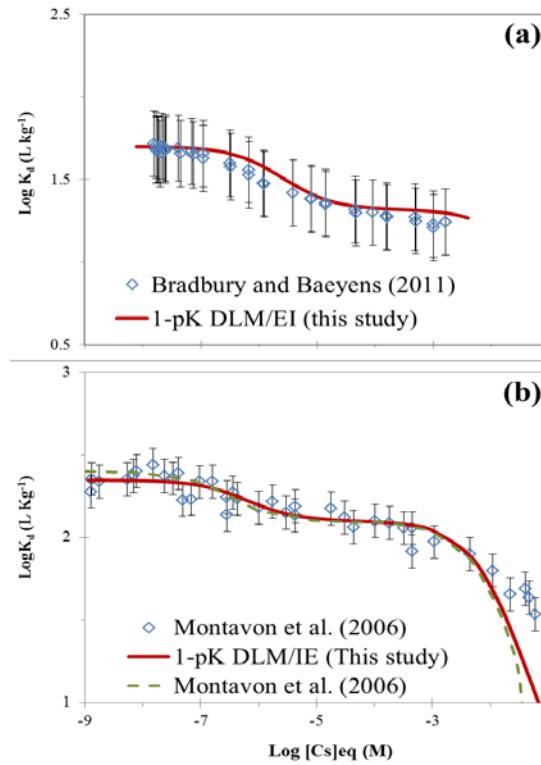
Hanford sediments

2.7% I



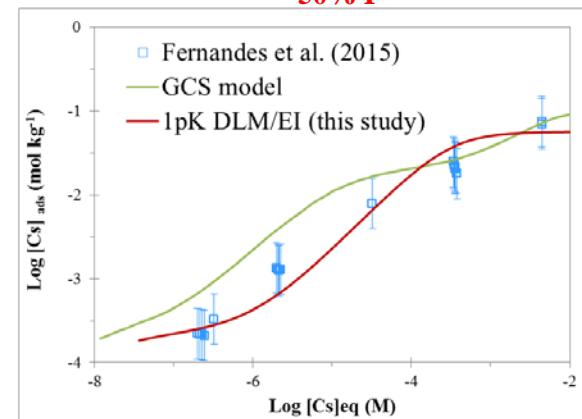
MX-80 bentonite

≈ 84% M



Boda clay

50% I



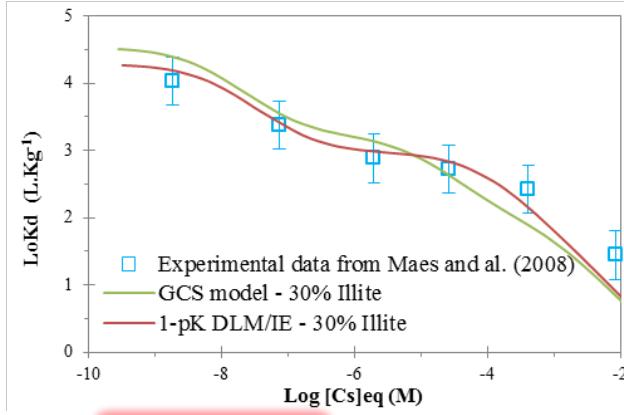
**RMSD = 0.25
R² = 0.80**

**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

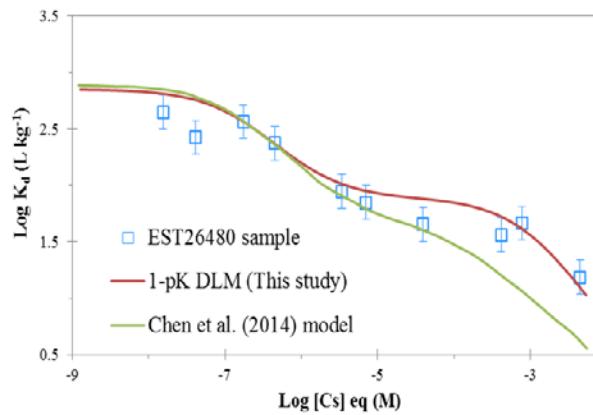


RMSD = 0.35
 $R^2 = 0.98$

RMSD = 0.51
 $R^2 = 0.96$

Callovo-Oxfordian sample 1

33% I + 14% M

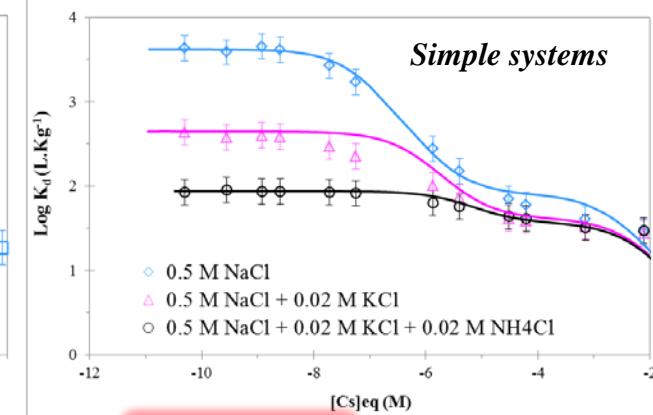


RMSD = 0.24
 $R^2 = 0.88$

RMSD = 0.40
 $R^2 = 0.92$

San Juan clay

40% I + 10% M + 12% K

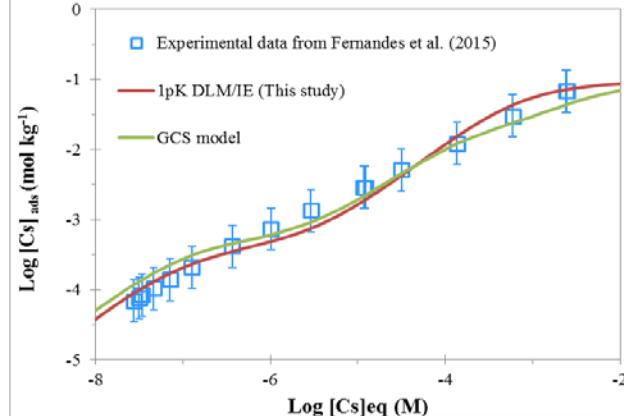


RMSD = 0.12
 $R^2 = 0.98$

RMSD = 0.22
 $R^2 = 0.93$

Opalinus clay

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

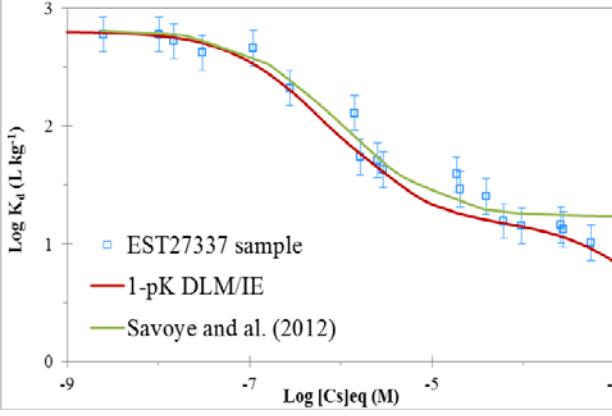


RMSD = 0.25
 $R^2 = 0.99$

RMSD = 0.23
 $R^2 = 0.99$

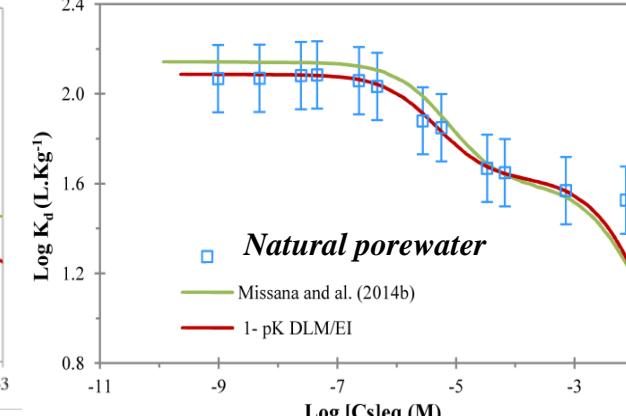
Callovo-Oxfordian sample 2

49% I + 15% M



RMSD = 0.22
 $R^2 = 0.99$

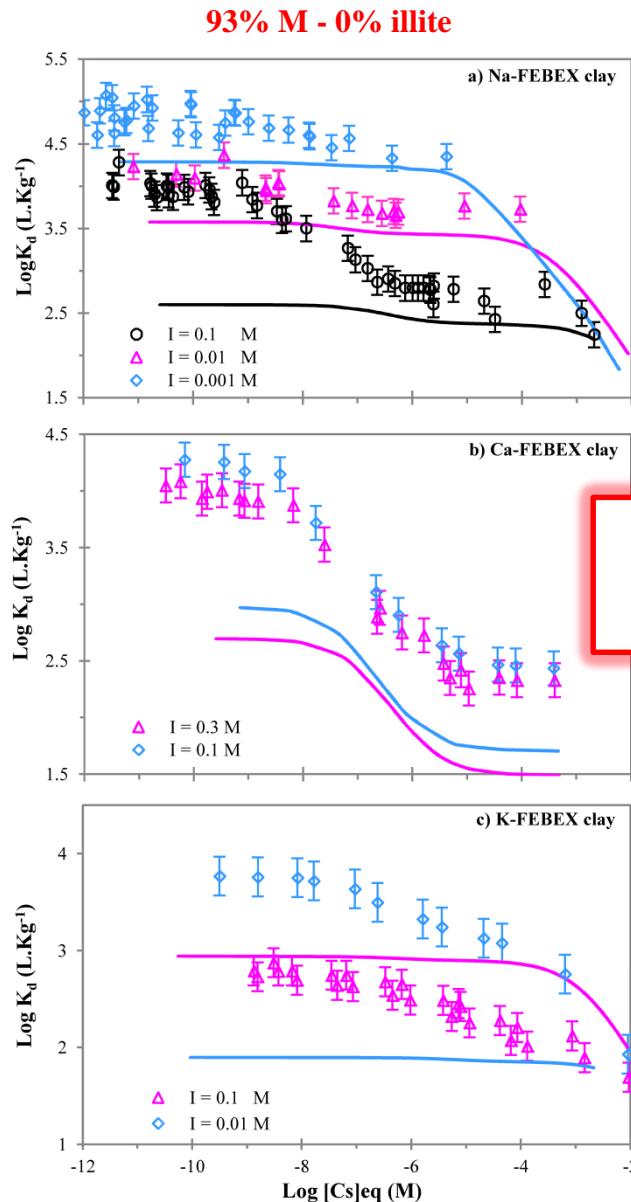
RMSD = 0.22
 $R^2 = 0.89$



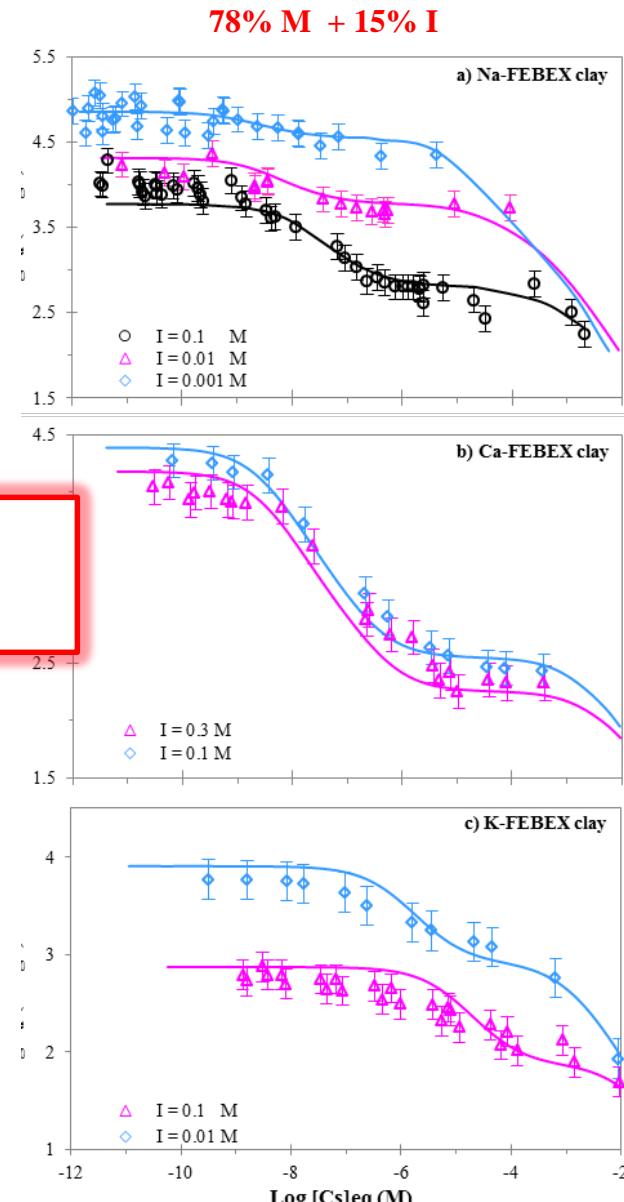
RMSD = 0.10
 $R^2 = 0.99$

RMSD = 0.11
 $R^2 = 0.99$

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



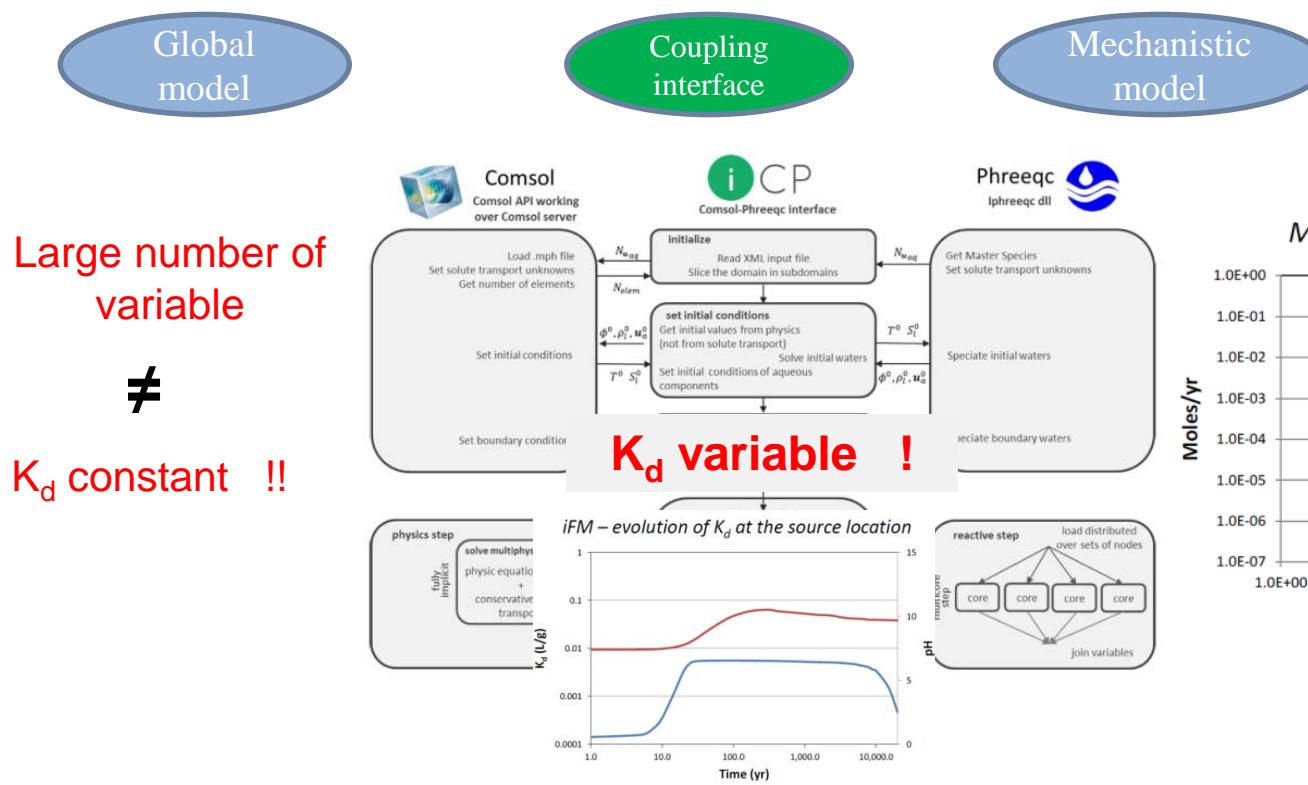
RMSD = 0.18
 $R^2 = 0.87$
 $n = 560$



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.



**THANK YOU FOR
YOUR ATTENTION**

GOLDSCHMIDT

YOKOHAMA 2016

26 JUNE - 1 JULY