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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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Context & objective

*Pure clay
minerals*

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

*natural clay
materials*

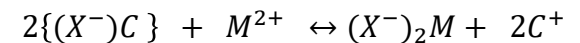
*Testing & Application of developed model using component
additivity (CA) approach*

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,



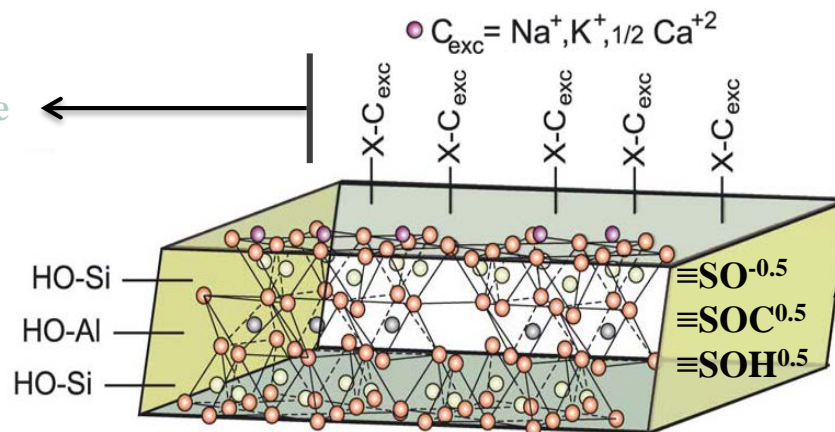
Mechanistic approach and model choice

| 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 |

Values determined by fitting experimental data (this study)

| 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 |

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

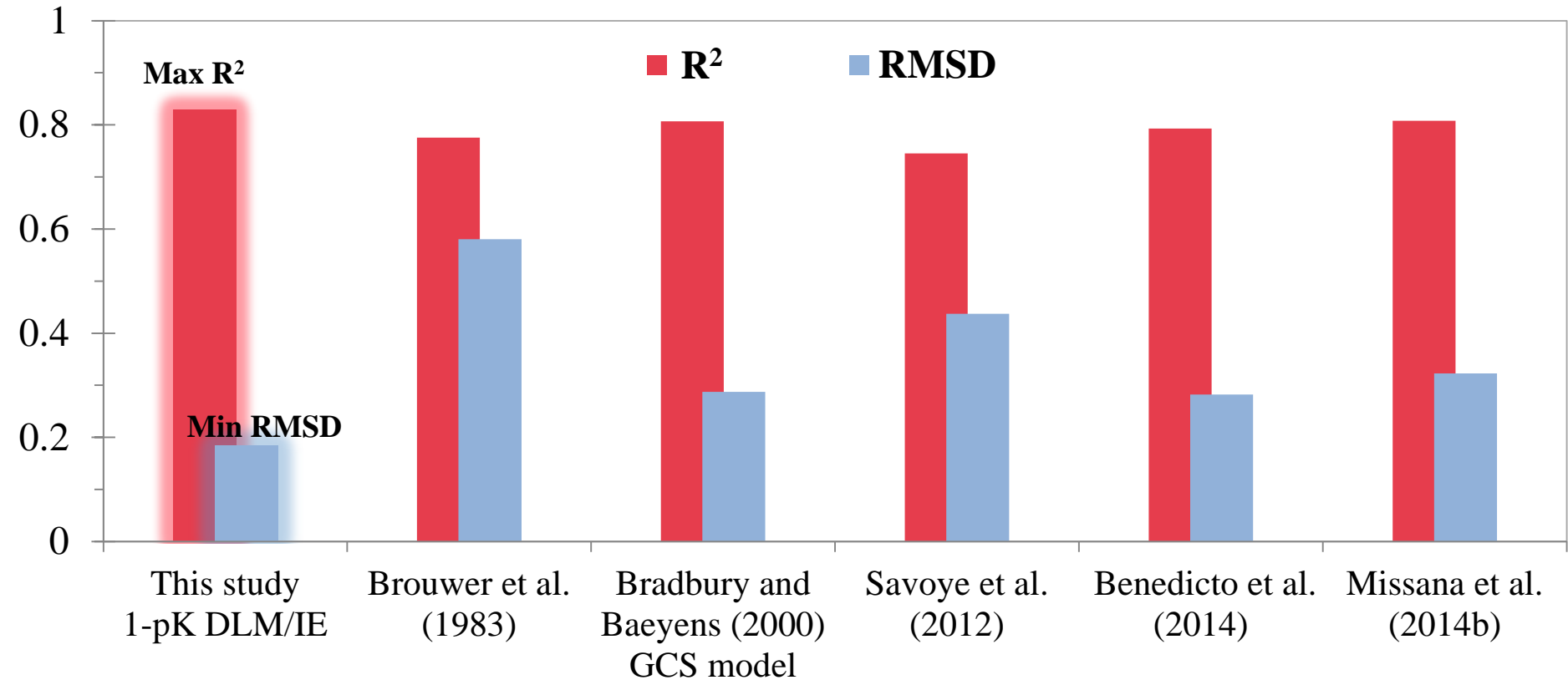
(n = 321 observations)

| 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

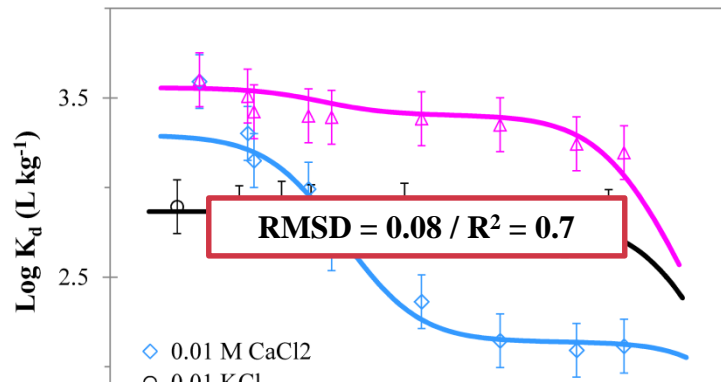


RMSD : Root Mean Square Deviation ; R^2 : Determination coefficient

Calibration, simulation results and confrontations

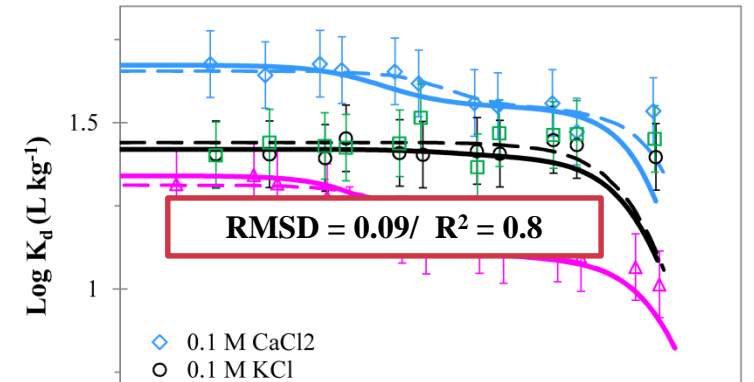
Montmorillonite

a) Sorption isotherms



Kaolinite

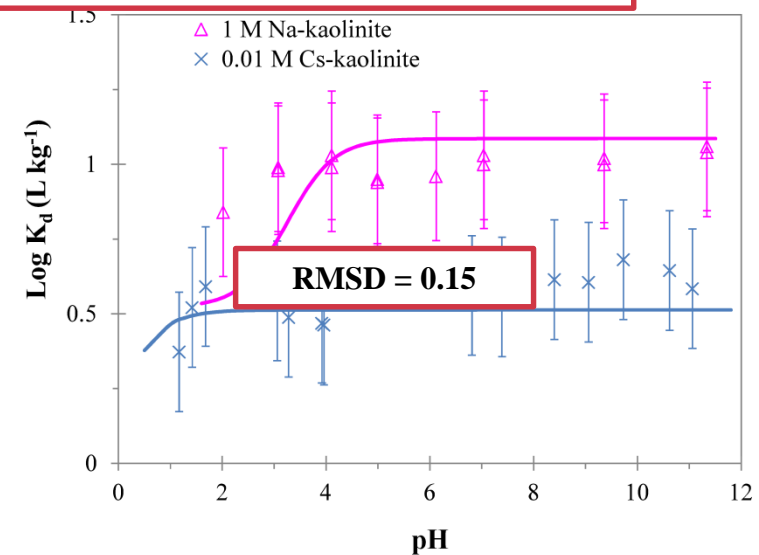
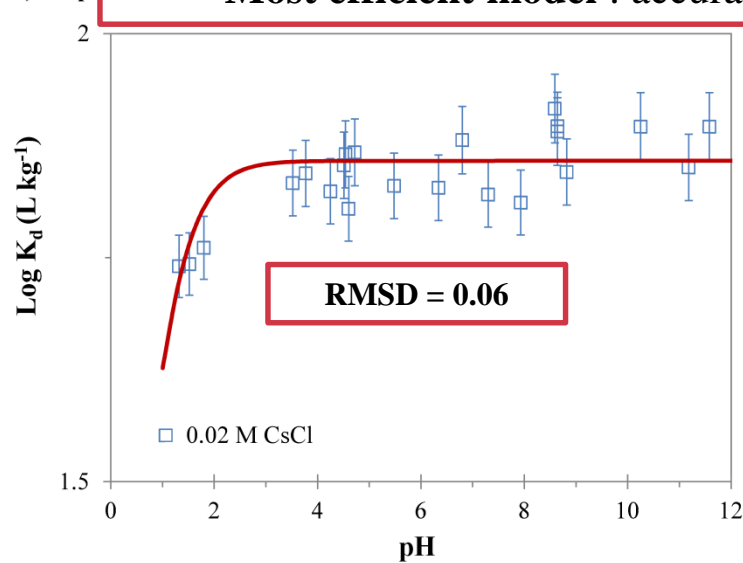
a) Sorption isotherms



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

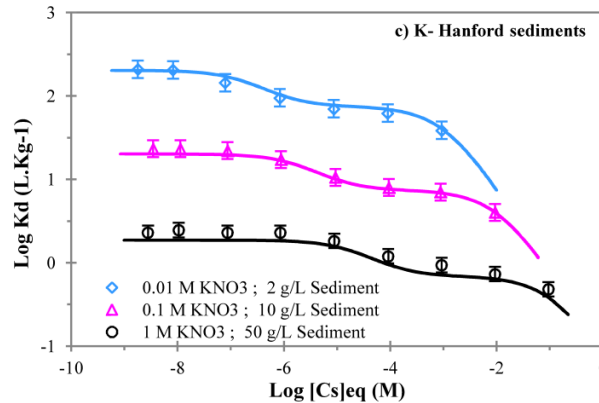
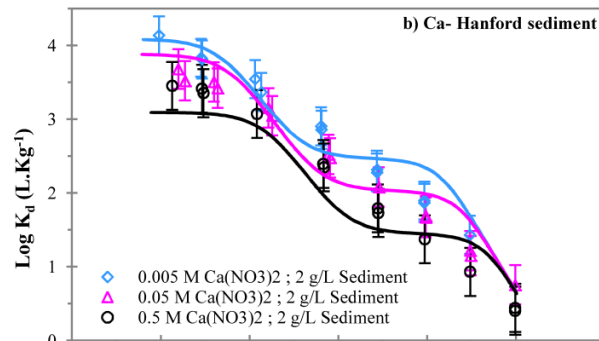
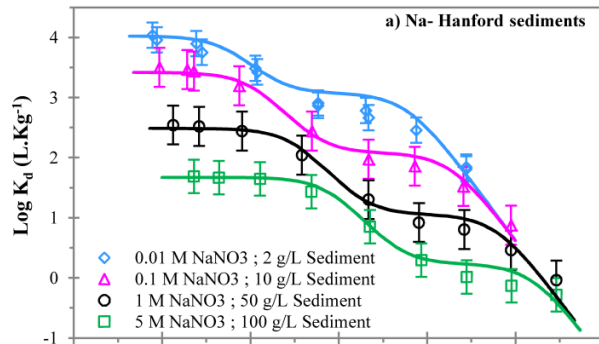
| | | | | | | |
|-------------------|--|------------------------------------|---|--------------|-----|---|
| FEDEX bentonite | Missana et al. (2014a) | 93% I/M with 15-10 % I | Simple conditions | 0.001-0.3 | 7 | 10 ⁻⁹ - 10 ⁻² |
| Callovo–Oxfordian | Chen et al. (2014) | I + M + (I/M) variable | Natural 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

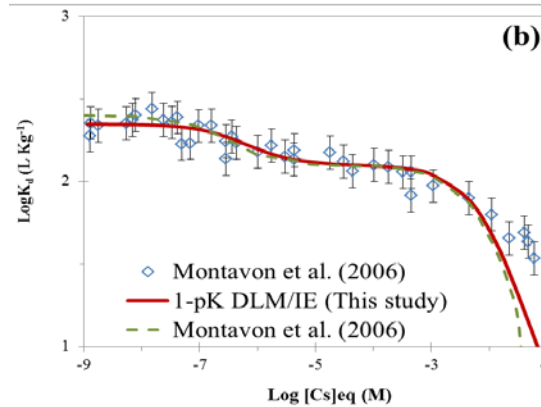
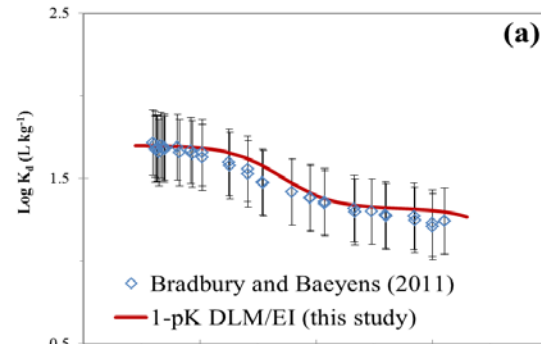
Hanford sediments

2.7% I



MX-80 bentonite

≈ 84% M

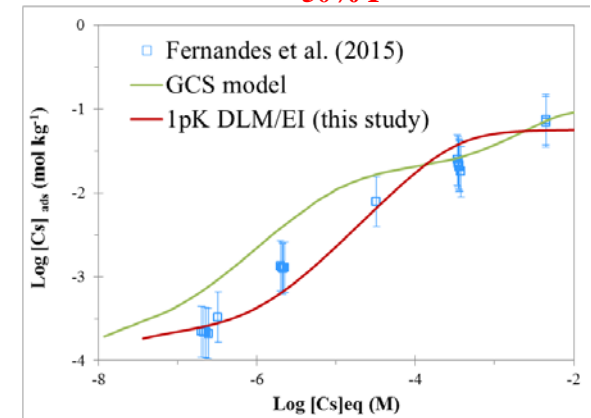


RMSD = 0.12
R² = 0.92

RMSD = 0.21
R² = 0.88

Boda clay

50% I



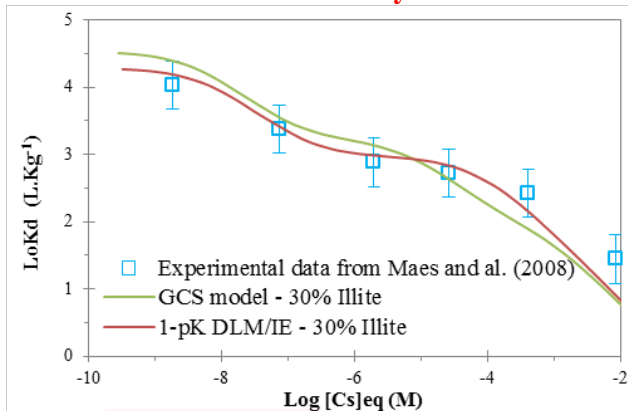
RMSD = 0.25
R² = 0.80

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

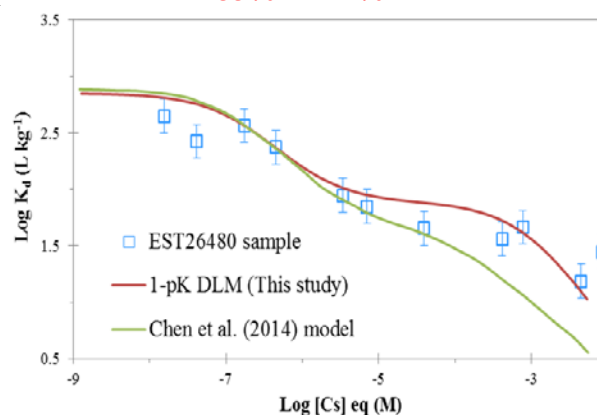


RMSD = 0.35
R² = 0.98

RMSD = 0.51
R² = 0.96

Callovo–Oxfordian sample 1

33% I + 14% M

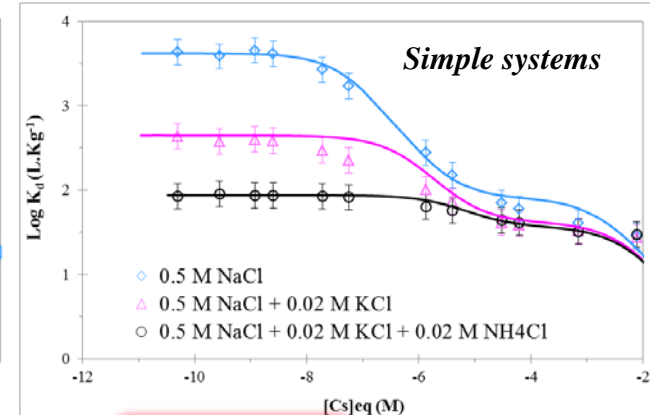


RMSD = 0.24
R² = 0.88

RMSD = 0.40
R² = 0.92

San Juan clay

40% I + 10% M + 12% K

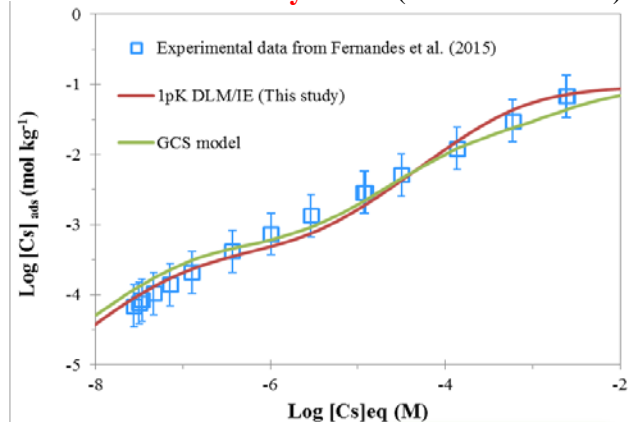


RMSD = 0.12
R² = 0.98

RMSD = 0.22
R² = 0.93

Opalinus clay

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

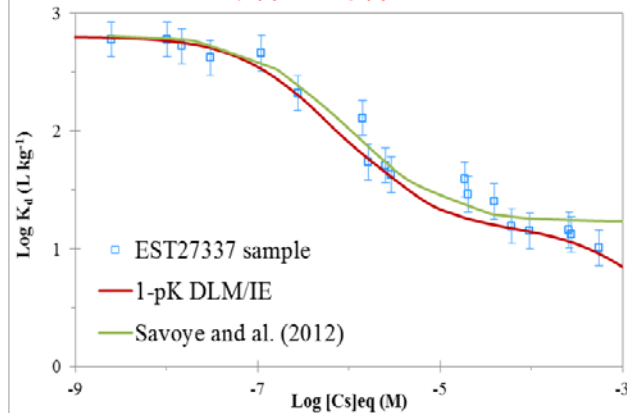


RMSD = 0.25
R² = 0.99

RMSD = 0.23
R² = 0.99

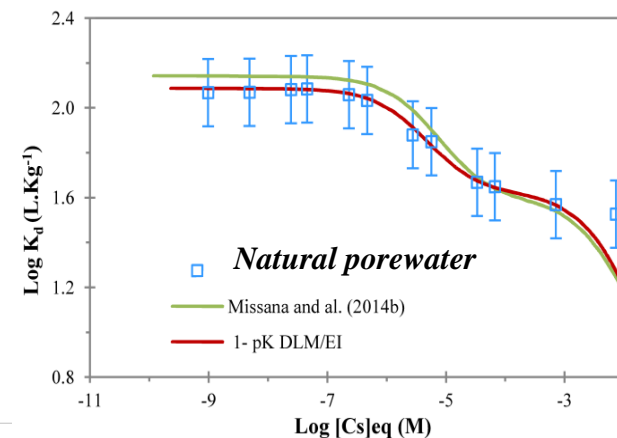
Callovo–Oxfordian sample 2

49% I + 15% M



RMSD = 0.22
R² = 0.99

RMSD = 0.22
R² = 0.89

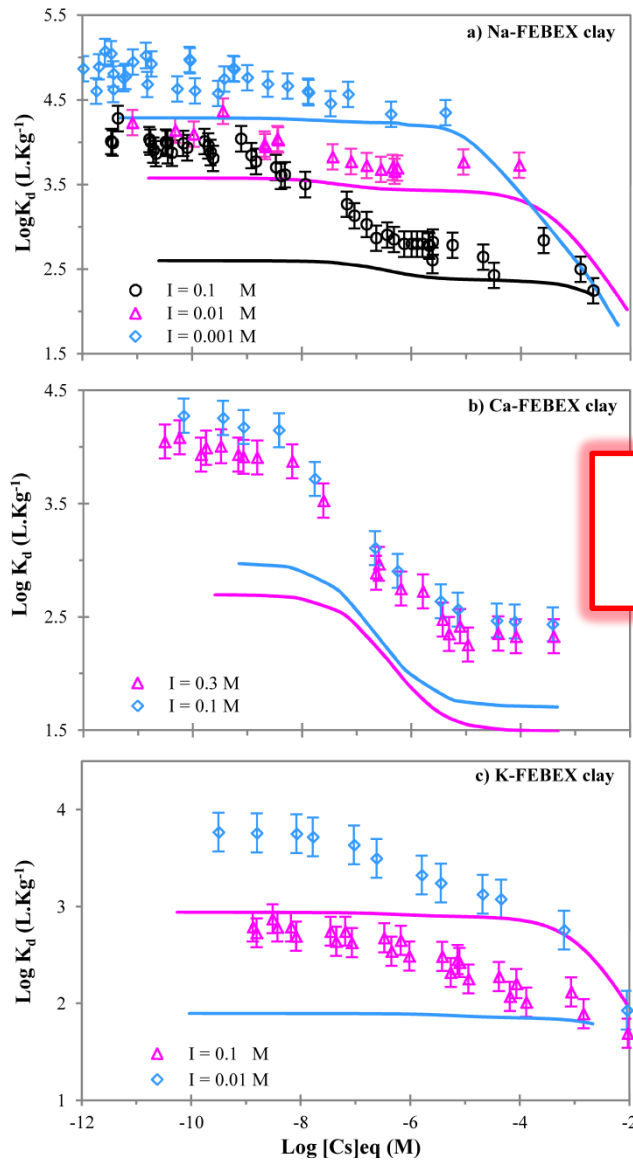


RMSD = 0.10
R² = 0.99

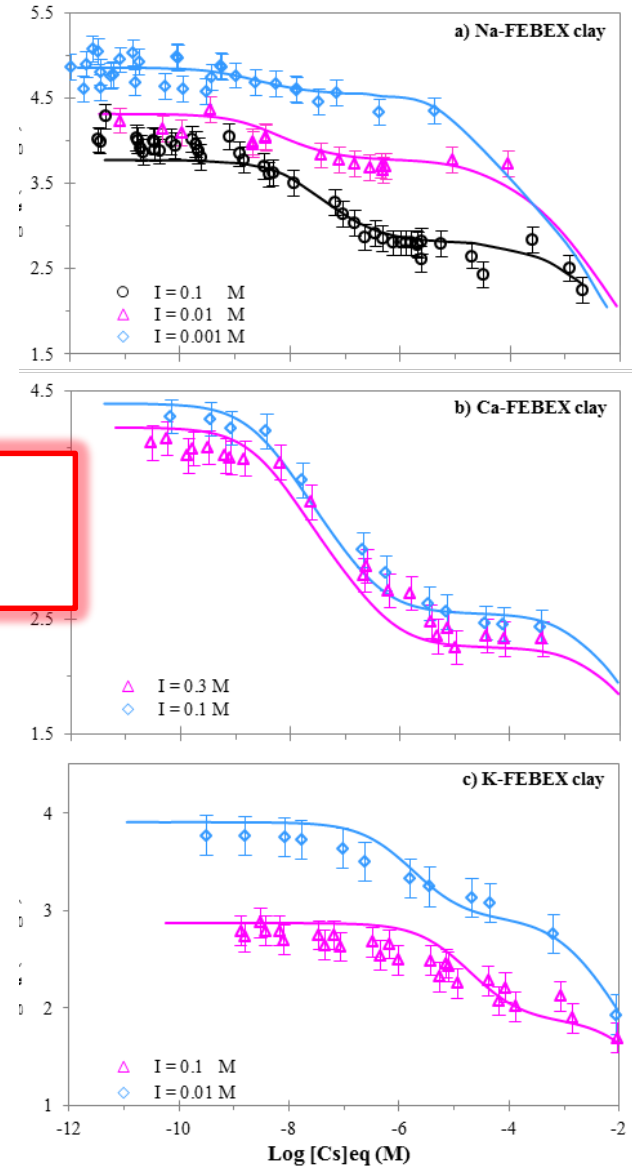
RMSD = 0.11
R² = 0.99

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
 $R^2 = 0.87$
 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.



Global model

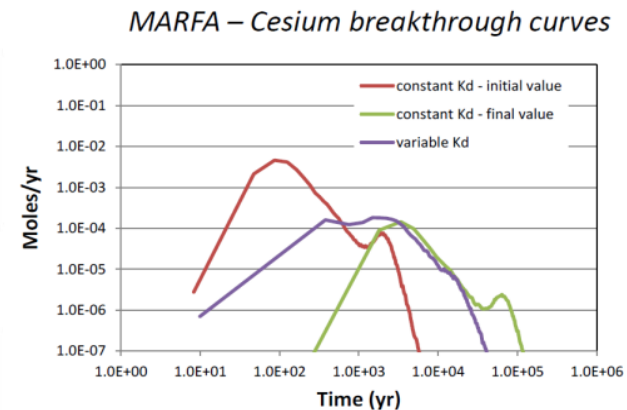
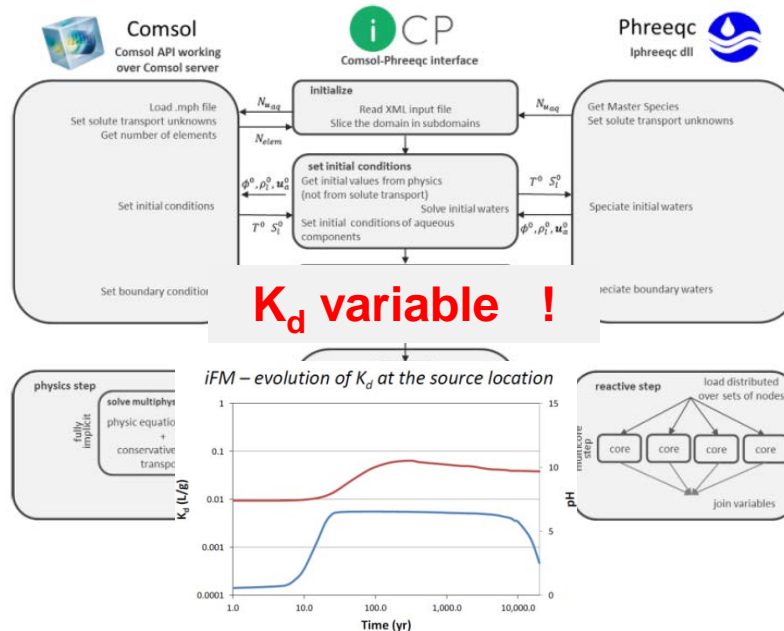
Coupling interface

Mechanistic model

Large number of variable

≠

K_d constant !!



***THANK YOU FOR
YOUR ATTENTION***

GOLDSCHMIDT
YOKOHAMA 2016
26 JUNE - 1 JULY