



*Supplement of*

## **Impact of the heterogeneity of the sandy Opalinus clay facies at the Mont Terri underground research laboratory on radionuclide migration**

**Naila Ait-Mouheb et al.**

*Correspondence to:* Naila Ait-Mouheb (n.ait.mouheb@fz-juelich.de)

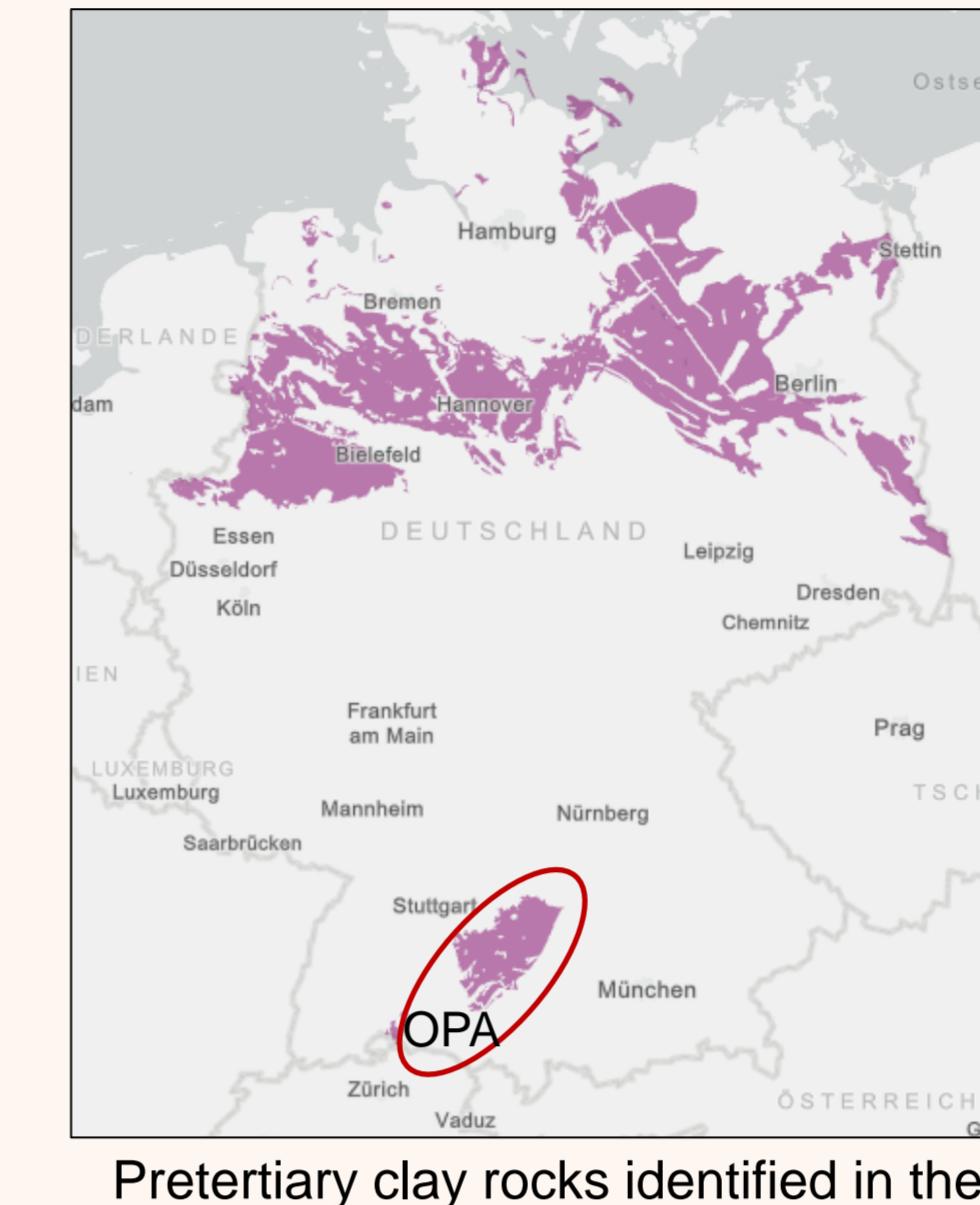
The copyright of individual parts of the supplement might differ from the article licence.

Naila Ait-Mouheb<sup>1,\*</sup>, Luc R. Van Loon<sup>2</sup>, Martin A. Glaus<sup>2</sup>, Yuankai Yang<sup>1</sup>,  
Guido Deissmann<sup>1</sup>, Dirk Bosbach<sup>1</sup><sup>1</sup>Institute of Energy and Climate Research – IEK-6, Forschungszentrum Jülich GmbH, 52425 Jülich – Germany<sup>2</sup>Laboratory for Waste Management, Paul Scherrer Institut, CH-5232 Villigen PSI – Switzerland

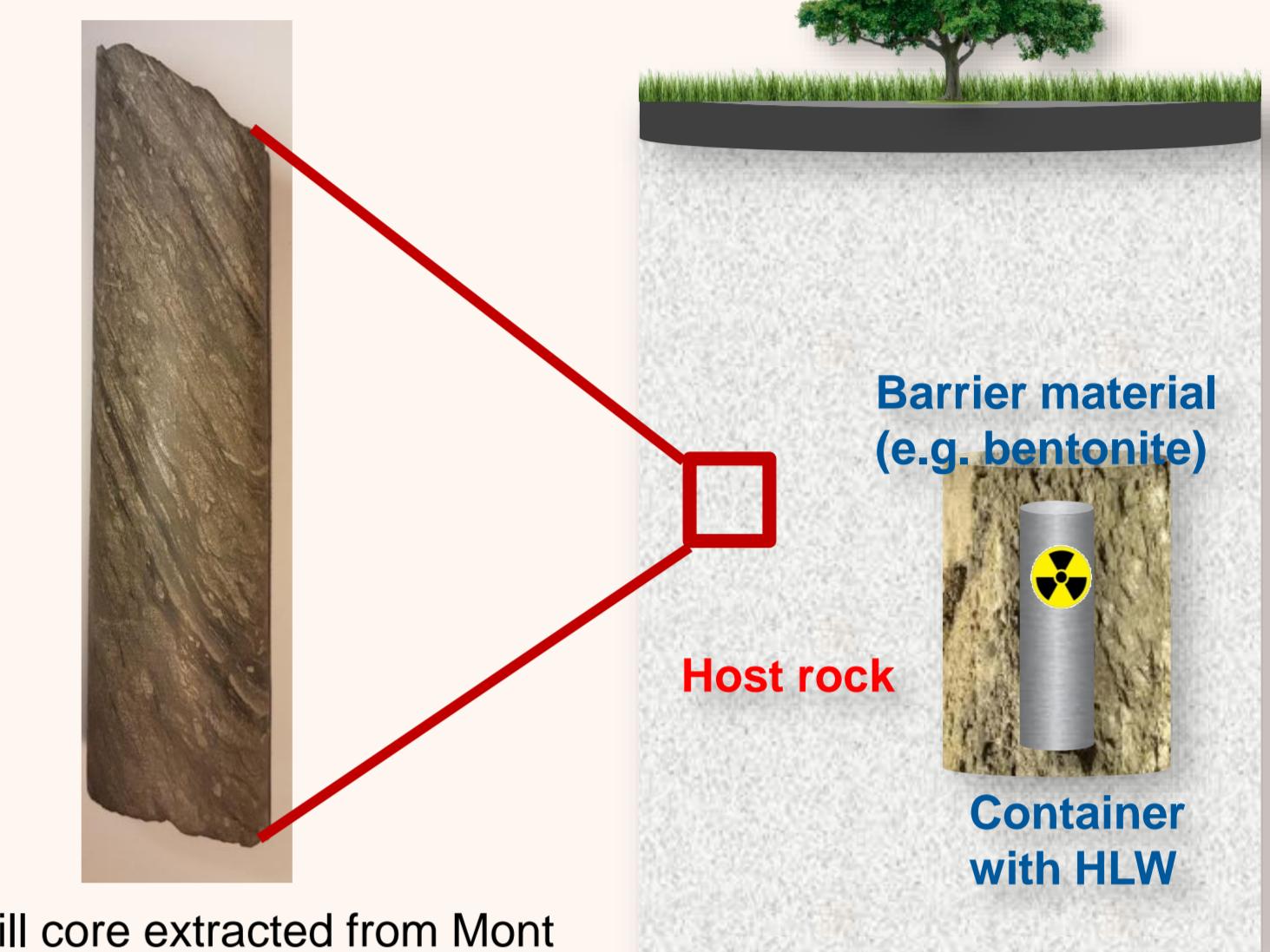
### Background / Objectives

- Within the site selection procedure for a repository for heat-generating, high-level radioactive wastes, the site with the "best-possible safety" is to be determined in a multi-phased comparative process.
- Potential host rocks for nuclear waste repositories are heterogeneous on various scales, ranging from nano-scale to kilometer-scale.
- Objective: Evaluation of the effects of structural and mineralogical heterogeneity of a clay host rock on  $^{226}\text{Ra}$  (half-life 1600 years) migration using sandy Opalinus Clay (OPA) facies as example.

Argillaceous clay rock formations



Pretertiary clay rocks identified in the "Zwischenbericht Teilgebiete" (www.bge.de)



Drill core extracted from Mont Terri underground laboratory

### Tools / Methods

- Chemical / structural characterization:**  
e.g., XRD, SEM-EDX,  $\text{N}_2$ -BET, quantitative Rietveld phase analysis using GSAS-II software.
- Determination of transport parameters:**  
Determination of HTO effective diffusion coefficient  $D_e$  and HTO connected porosity  $\varepsilon_c$  using diffusion cells [1].

#### Sorption experiments ( $^{226}\text{Ra}$ ):

Batch sorption experiments with different samples representative of the heterogeneity of the drill cores, S/L ratio = 117 g·L<sup>-1</sup>,  $^{226}\text{Ra}$  analysis by liquid scintillation counting (LSC).

#### Modelling sorption data (bottom-up approach):

Phreeqc 3.6 [2] assuming that illite and illite/smectite mixed layers are the main sorbing phases in the sandy OPA (cf. [3]).

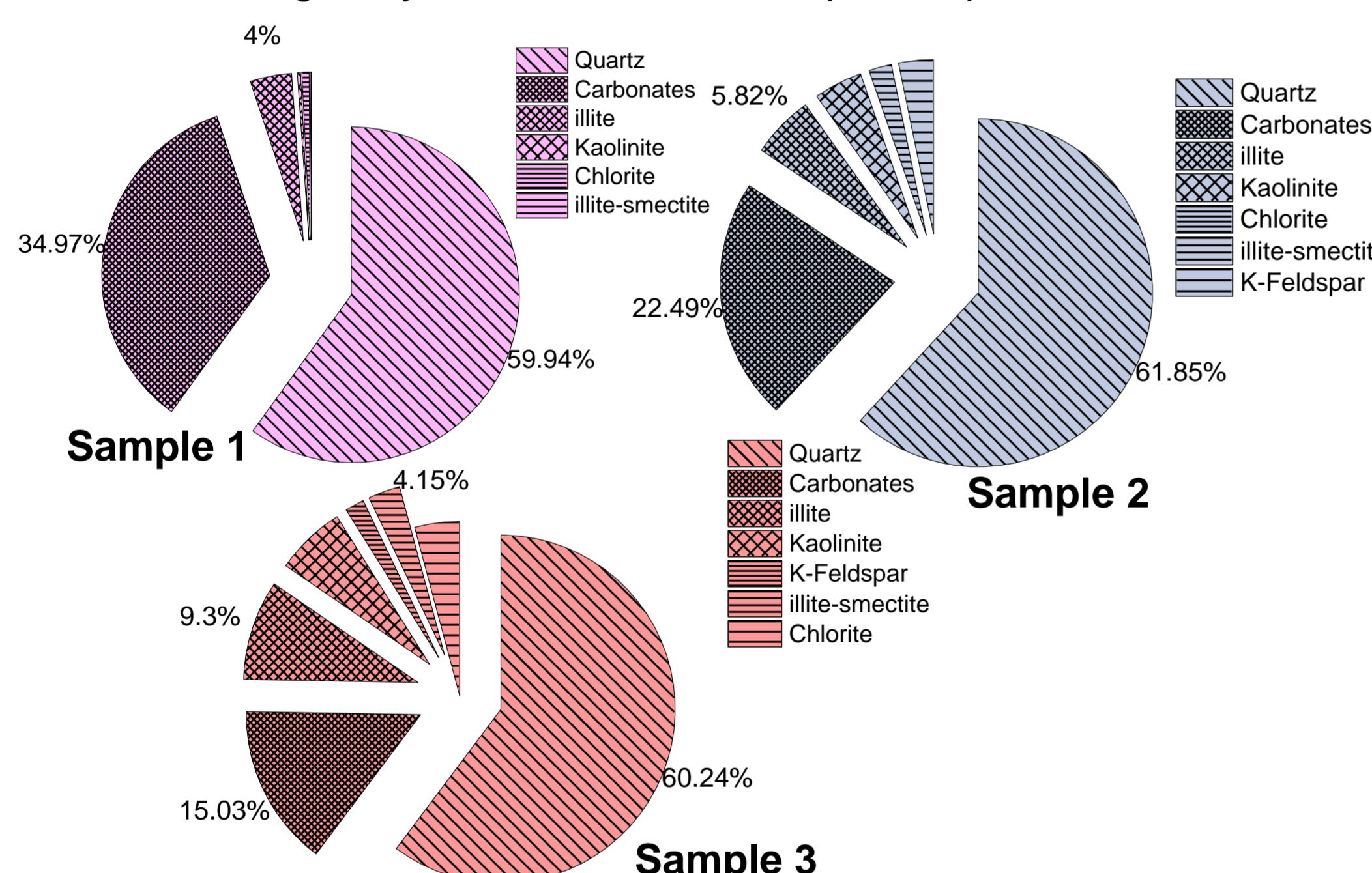
#### Blind reactive transport modelling of $^{226}\text{Ra}$ migration in sandy OPA

- ICP 1.6 [4], Phreeqc 3.6 [2], Comsol Multiphysics 5.5 [5],
- Thermochimie database V10a,
- Retention of  $^{226}\text{Ra}$  is taken into account via cation exchange, surface complexation reactions and the formation of solid solutions of (Ra,Ba,Sr)-sulphates.

### Selected results

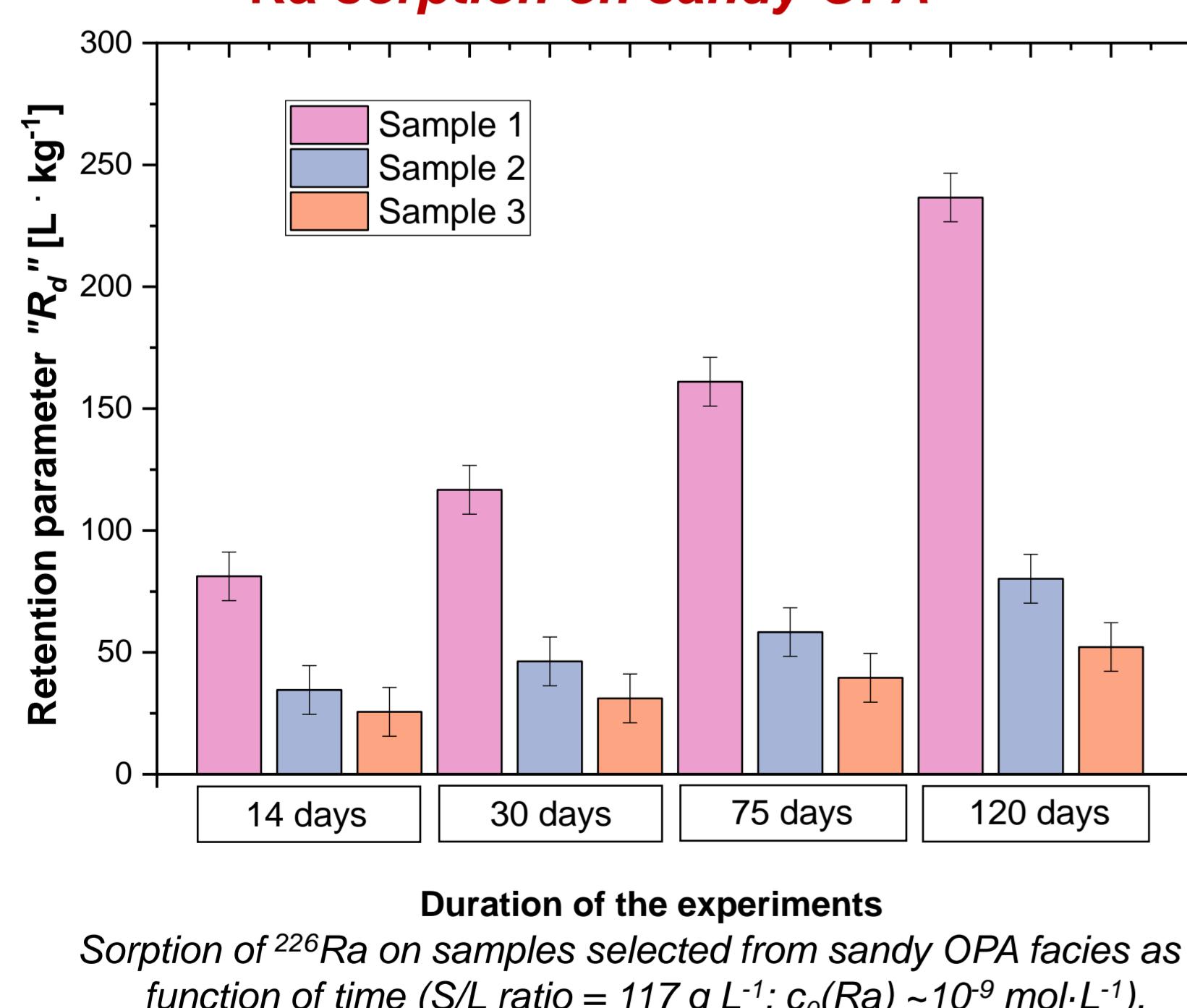
#### Characterization of sandy OPA

Mineralogical composition (wt.%) of powdered samples representative of the heterogeneity of the core used in sorption experiments



→ Minor phases: pyrite, siderite, feldspar, and rutile  
→ (Ba, Sr) sulphate solid solutions embedded in clay matrix

#### $^{226}\text{Ra}$ sorption on sandy OPA



→  $20 \text{ L} \cdot \text{kg}^{-1} < \text{R}_d(^{226}\text{Ra}) < 125 \text{ L} \cdot \text{kg}^{-1}$  (after 30 days)

→ Increase of  $^{226}\text{Ra}$  retention over time and with increasing carbonate content

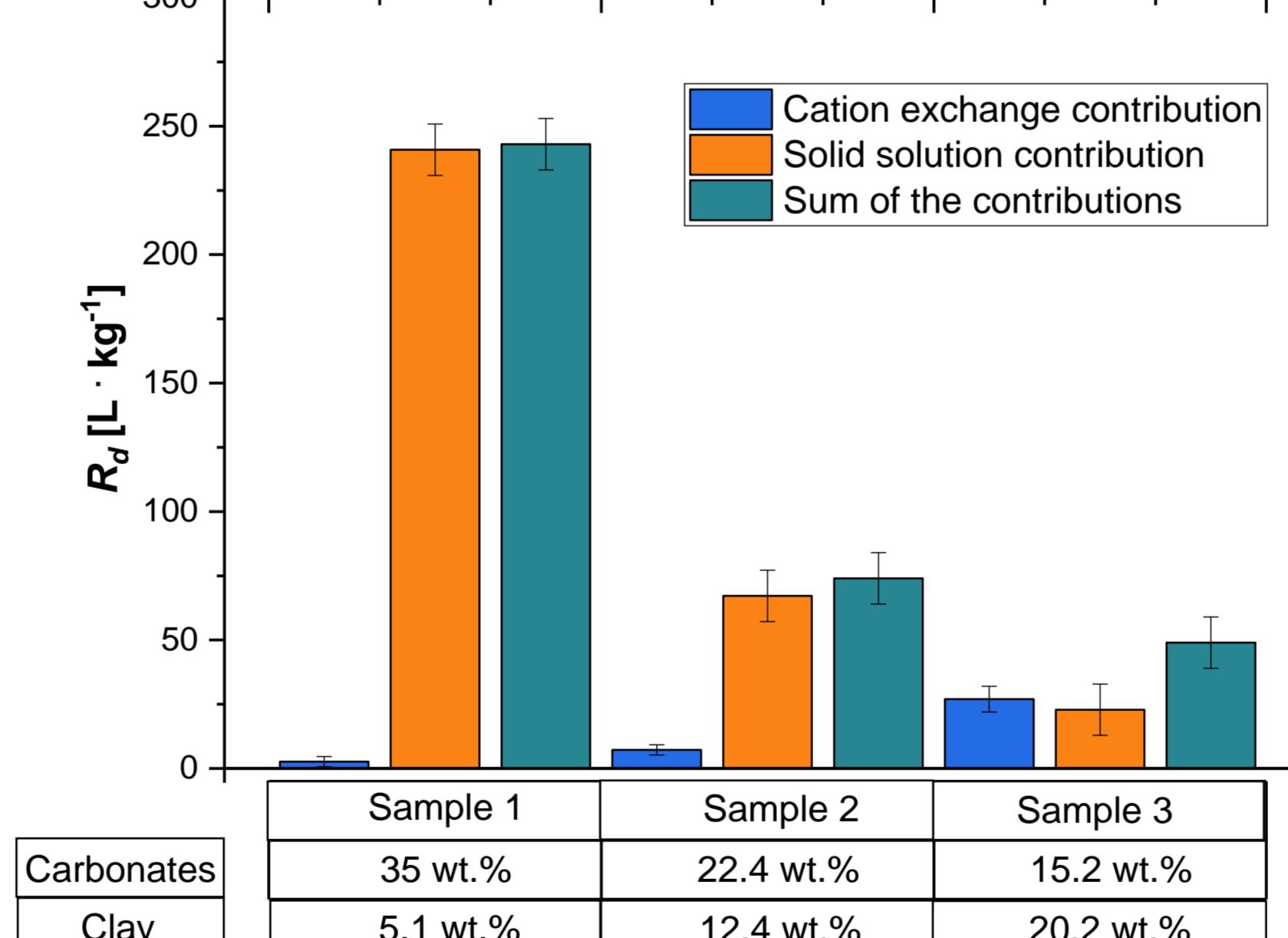
→ Diffusion or incorporation of  $^{226}\text{Ra}$  into minerals (e.g., calcite) indicated

#### $^{226}\text{Ra}$ sorption modelling (bottom-up approach)

| Surface complexation reaction   | Reference |
|---|-----------|
| $\equiv \text{clay-OH} + \text{Ra}^{2+} \rightleftharpoons \equiv \text{clay-ORa}^+ + \text{H}^+$ | [7]       |
| Cation exchange reaction  |           |
| $2\text{Na}^+ \text{ clay} + \text{Ra}^{2+} \rightleftharpoons \text{Ra-clay} + 2\text{Na}^+$     | [7]       |

- Site types, site capacities, and protolysis constants for illite [6]
- Parameters for  $^{226}\text{Ra}$  sorption on pure clay phases [7]

Different contributions to  $^{226}\text{Ra}$  retention in sandy OPA after 120 days equilibration time



→ The results show a major contribution on  $^{226}\text{Ra}$  retention due to formation of Ba-Sr-Ra carbonates and sulfate solid solutions and a smaller contribution due to surface complexation and cation exchange.

#### Prediction of $^{226}\text{Ra}$ migration in sandy OPA

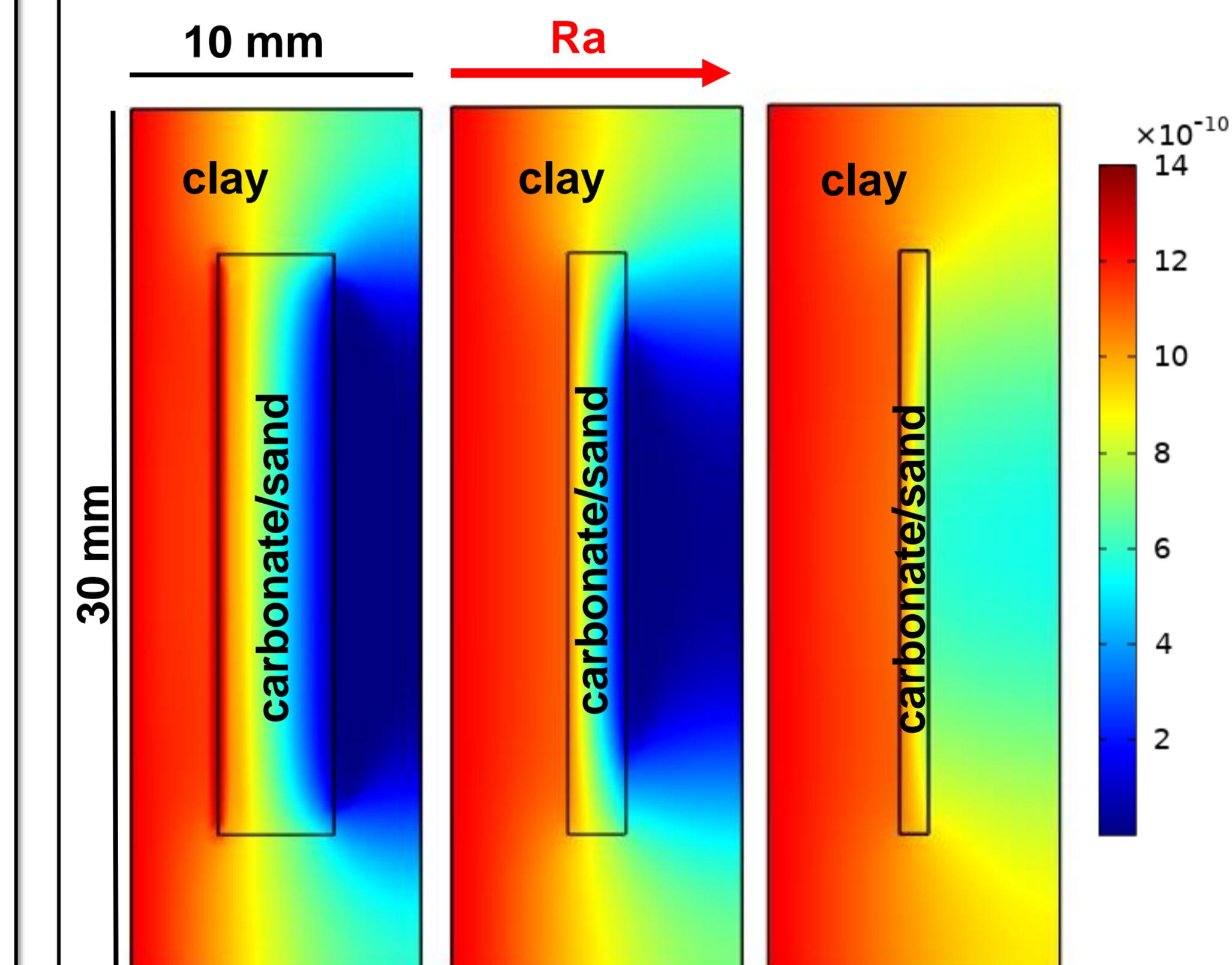
- Site types, site capacities, and protolysis constants for illite [6]
- Parameters for  $^{226}\text{Ra}$  sorption on pure clay phases [7]
- Clay water saturated with calcite, dolomite, celestine and barite
- Boundary conditions: left → fixed concentration, right → closed

##### Clay layer:

- $\text{CEC} = 106 \cdot 10^{-3} \text{ eq kg}^{-1}$  OPA  
 $D_e = 4 \cdot 10^{-11} \text{ m}^2/\text{s}$ , porosity  $\varepsilon = 0.16$  [8]
- (Ra,Ba,Sr)-sulphate solid solution formation in equilibrium with clay water

##### Carbonate/sand lens:

- Porosity  $\varepsilon = 0.08$  [9]
- $D_e = 2 \cdot 10^{-12} \text{ m}^2/\text{s}$
- Different proportions of clay and carbonate/sand



Modelled diffusion profiles of  $^{226}\text{Ra}$  (mole/kg<sub>water</sub>) in sandy OPA after 10 days of in-diffusion.

→ The reactive transport model shows different diffusion profiles of  $^{226}\text{Ra}$  as a function of carbonate/sand content

### Conclusions

#### Characterization of sandy OPA samples

→ Heterogeneous composition with amounts of quartz, carbonates, and clay minerals varying from 58 to 65 wt.%, 13 to 35 wt.% and 5 to 25 wt.%, respectively.

#### Sorption parameters

→ Increase of  $^{226}\text{Ra}$  retention over time indicating

→ kinetically controlled sorption process.

→ Uptake of  $^{226}\text{Ra}$  associated with cation exchange, surface complexation reactions, and

→ Formation of solid solutions of  $^{226}\text{Ra}$  with (Ba, Sr)-sulphates and/or uptake by carbonate minerals.

→ Bottom-up approach for sorption modelling not applicable for  $^{226}\text{Ra}$  in clay rocks with high carbonate content.

#### Reactive transport model of Ra migration

→ The heterogeneity of OPA-SF affects the diffusive mass transport of  $^{226}\text{Ra}$ .