An experimental versus numerical approach to determine capability of Archie's law to explain impact of evolving porosity on diffusivity

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AN EXPERIMENTAL VERSUS NUMERICAL APPROACH TO DETERMINE CAPABILITY OF ARCHIE'S LAW TO EXPLAIN IMPACT OF EVOLVING POROSITY ON DIFFUSIVITY

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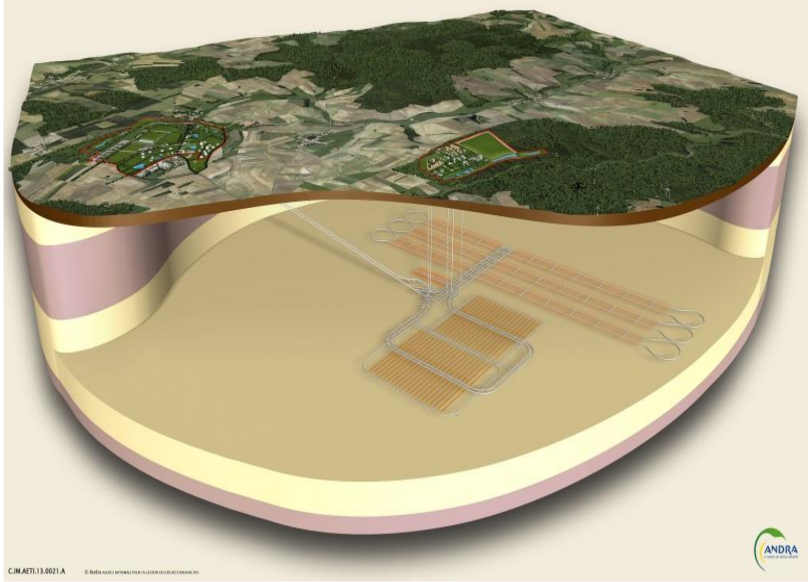
CONTEXT: DEEP GEOLOGICAL DISPOSAL OF RADIOACTIVE WASTES

ILW-HLW radioactive waste disposal facility



Properties of claystones

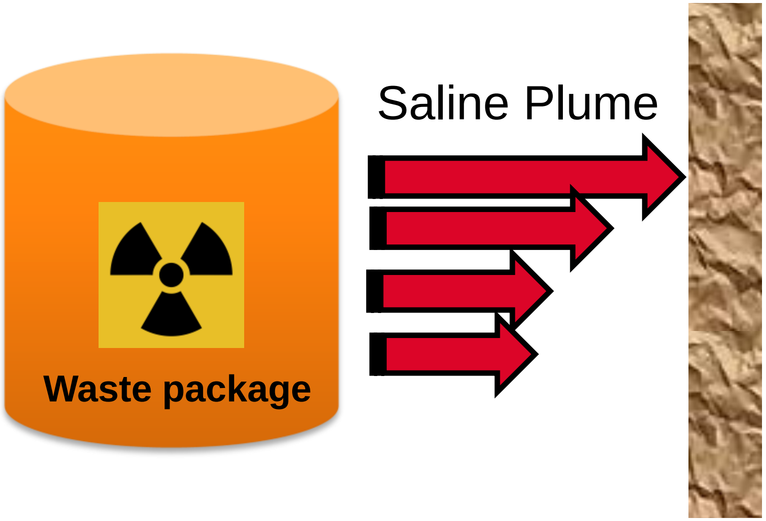
Very low permeability

➔Diffusion of ionic species

Negatively surface charged clayey minerals

➔Sorption of cationic species and exclusion of anionic species

Clay properties essential to delay radionuclide transport into surrounding geosphere

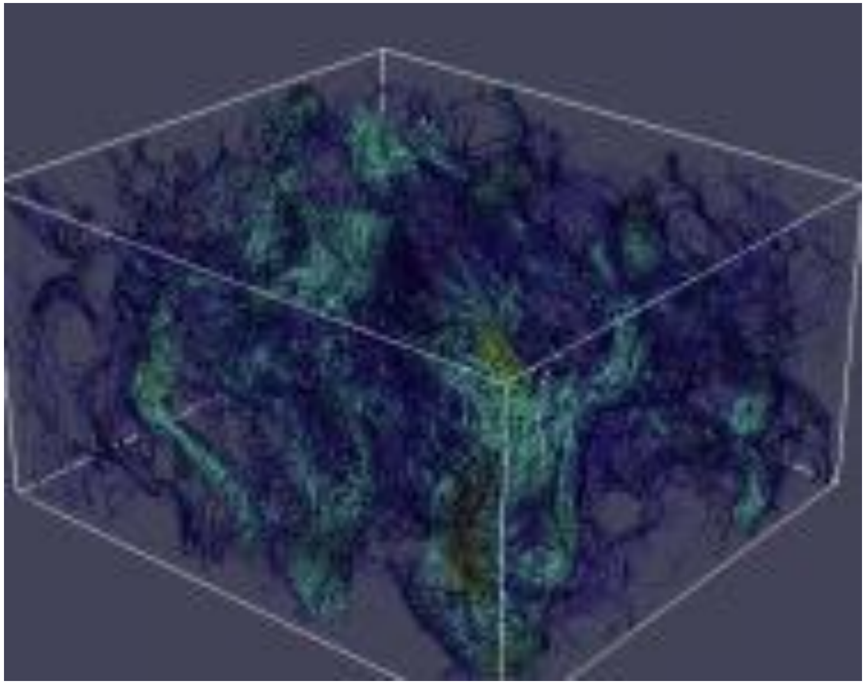


Change in rock containment properties due to mineral perturbation

How such chemical impacts observed at lab-scale can be extrapolated for repository space and time scales?

CONTEXT: CHEMISTRY TRANSPORT CODES AND LONG-TERM EVOLUTION

Porous system[1]



Porosity

$$\phi = \left(1 - \frac{\rho_d}{\rho_s}\right)$$

ρ_d (g.cm^{-3}) is the dry density
ρ_s (g.cm^{-3}) is the grain density

Mineral perturbation impact on diffusivity

Empirical Archie's law

$$\frac{D_e}{D_0} = \phi^m$$

m is the cementation factor (-) (property of intact porous material)
D_e is the effective diffusion coefficient (m^2.s^{-1})
D_o is the diffusion coefficient in bulk water (m^2.s^{-1})
ϕ is the porosity (-)

1) Gomrod *et al.* 2017

Can empirical Archie's law reproduce mineral perturbation impact on diffusivity for a complex system such as claystones?

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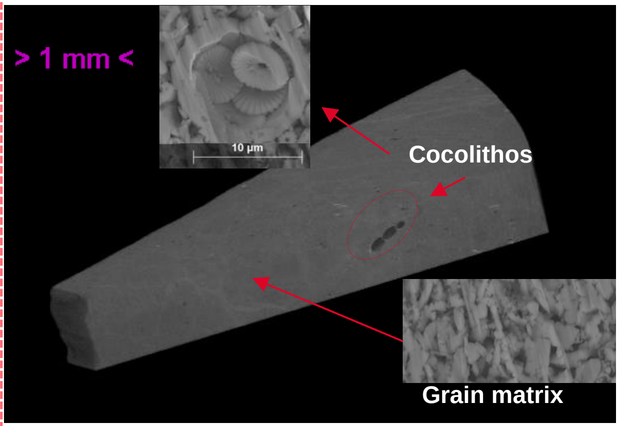
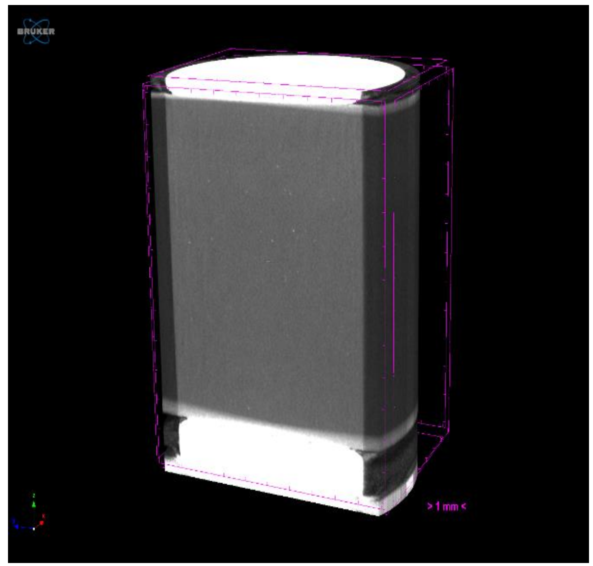
MATERIALS : THREE POROUS SYSTEMS

Compacted clay minerals

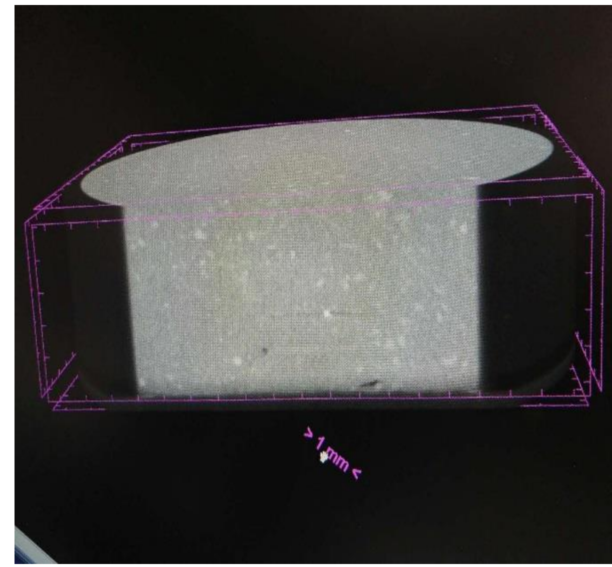
Micritic chalk



Kaolinite



Illite



Chalk properties

- ❑ 97% calcite matrix
- ❑ Total porosity:45%
- ❑ No alteration in cations/anions diffusion
- ❑ 2% of coccolithos as macro-porosity

Properties @ ρ_d=1.7 g.cm^{-3} (Kaolinite)

- ❑ Total porosity: 36 %
- ❑ Anionic accessible porosity: 36 %
- ❑ weak negative surface charge (CEC = 38 meq.kg^{-1})

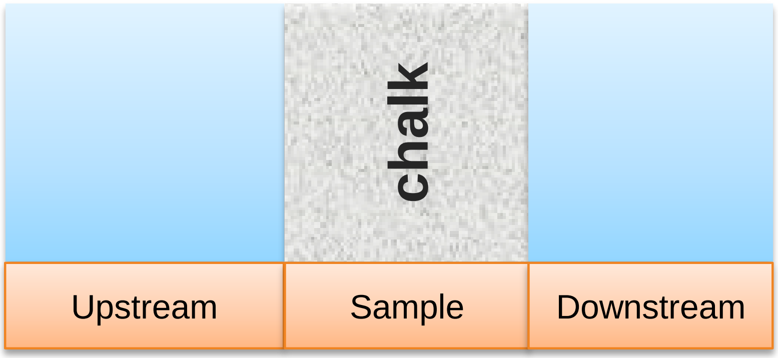
Properties @ ρ_d=1.9 g.cm^{-3} (Illite)

- ❑ Total porosity: 29 %
- ❑ Anion accessible porosity: 19%
- ❑ Negative surface charge (CEC = 225 meq.kg^{-1})

What is the impact of spatial variability on studied mineral perturbation and subsequently on diffusivity of water tracers?

METHOD: REACTIVE DIFFUSION SETUP

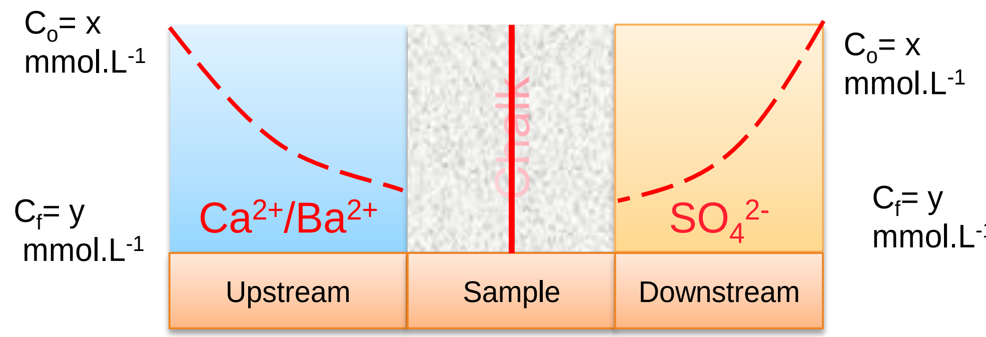
Reactive diffusion setup



Precipitation of two sulfate-alkaline minerals

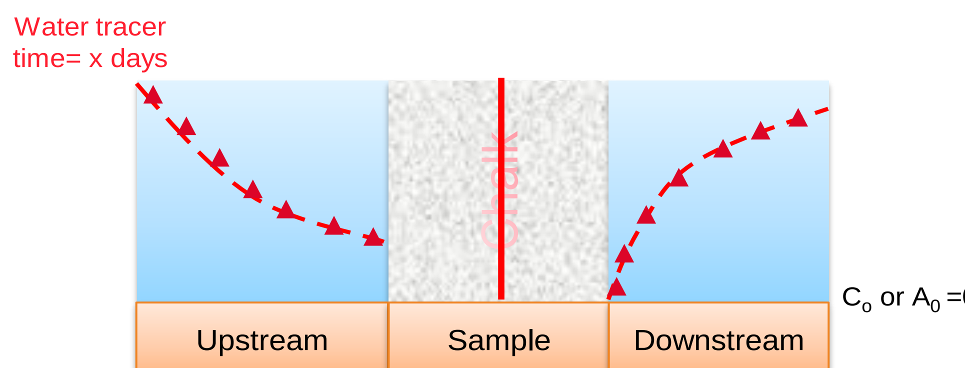
Barite Properties:	Gypsum Properties:
❖ Sparingly soluble ❖ Slow kinetics of precipitation	❖ Fairly soluble ❖ Fast kinetics of precipitaiton

Precipitation impact on total porosity



- Barite molar volume 74.5 $cm^3.mol^{-1}$
- Gypsum molar volume 52.5 $cm^3.mol^{-1}$

Precipitation impact on diffusivity



RESULTS: PRECIPITATION IMPACT ON TOTAL POROSITY AND DIFFUSIVITY

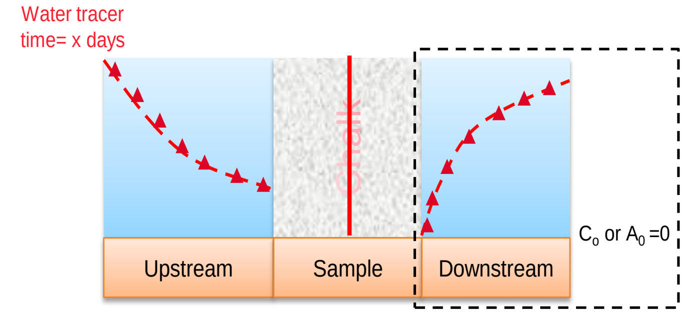
Precipitation impact on total porosity

End of Experiments:

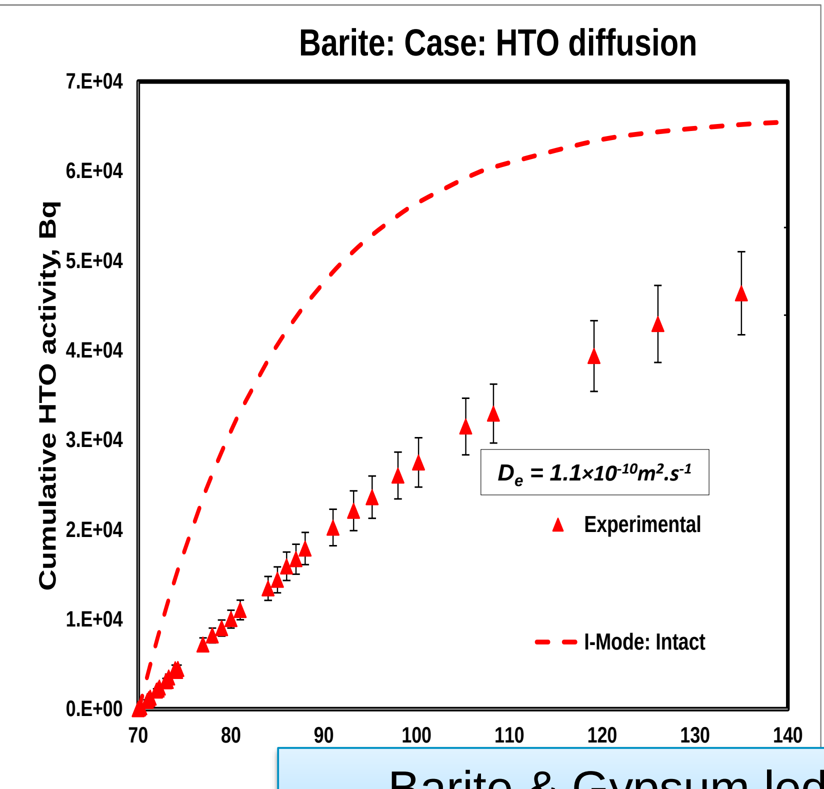
- **Barium contribution = 2.5 mmol**
- **Gypsum contribution = 1.5 mmol**

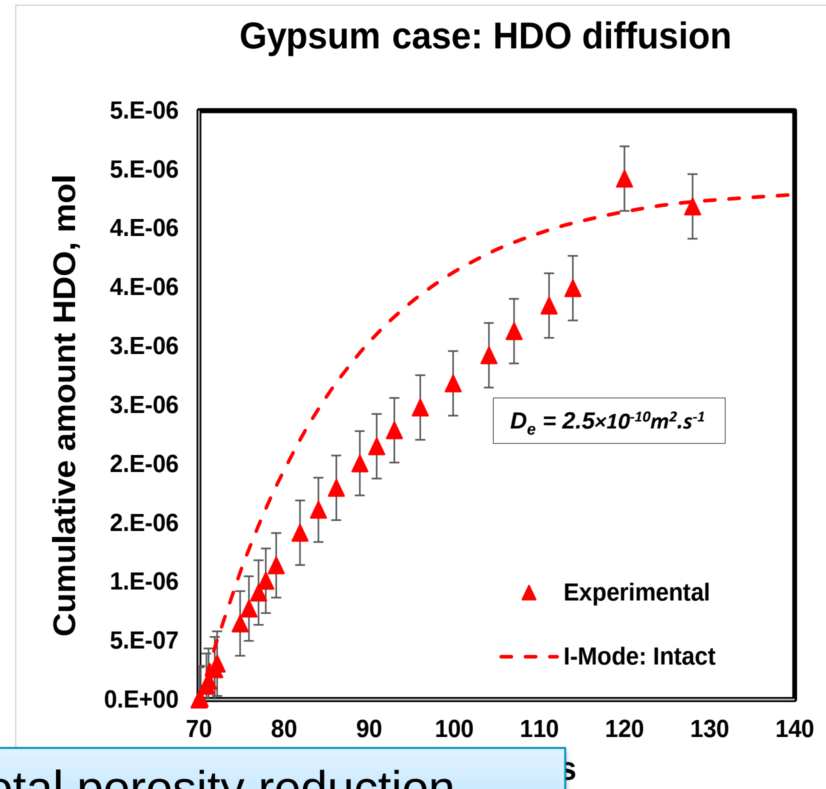
Total porosity reduction

- **Barite case = 2.5%**
- **Gypsum case = 2%**



Precipitation impact on diffusivity





Barite & Gypsum led to similar total porosity reduction
Why barite impact more on diffusivity than gypsum?

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RESULTS: CAN CODE REPRODUCE PRECIPITATION IMPACT ON TOTAL POROSITY AND DIFFUSIVITY?

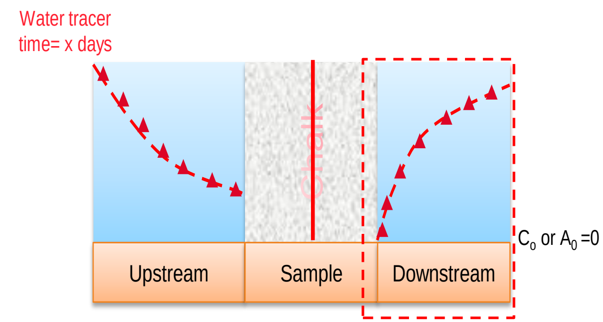
Code prediction: Reactant contribution to precipitation

End of Experiments:

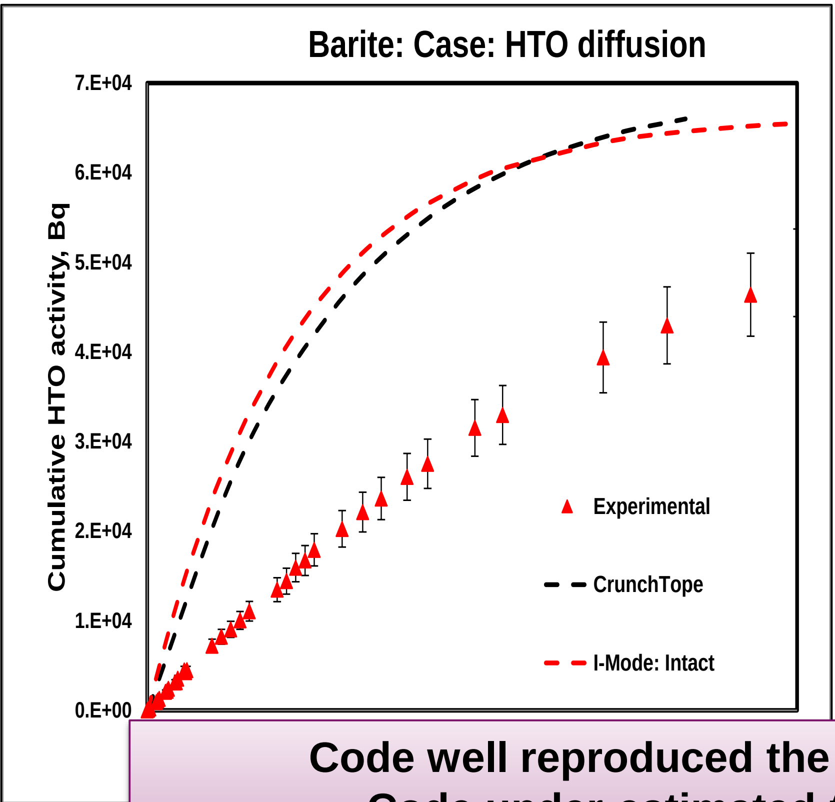
- **Barium contribution = 2.8 mmol**
- **Gypsum contribution = 1.5 mmol**

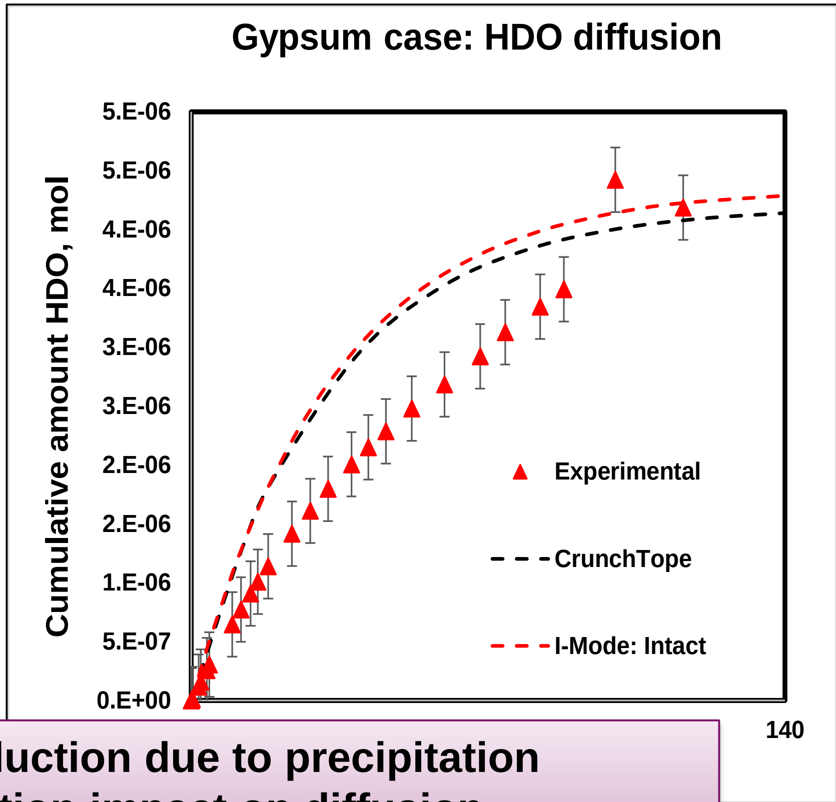
Total porosity reduction

- **Barite case ~ 2.6%**
- **Gypsum case ~ 2%**



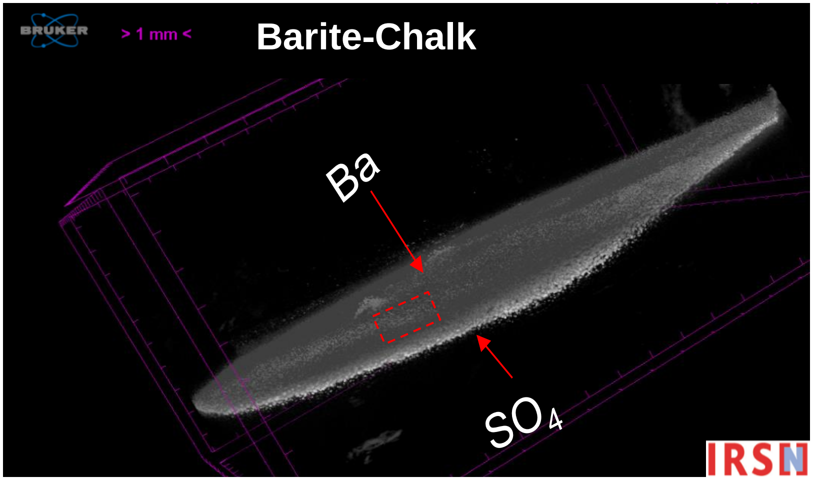
Code prediction: Precipitation impact on diffusivity

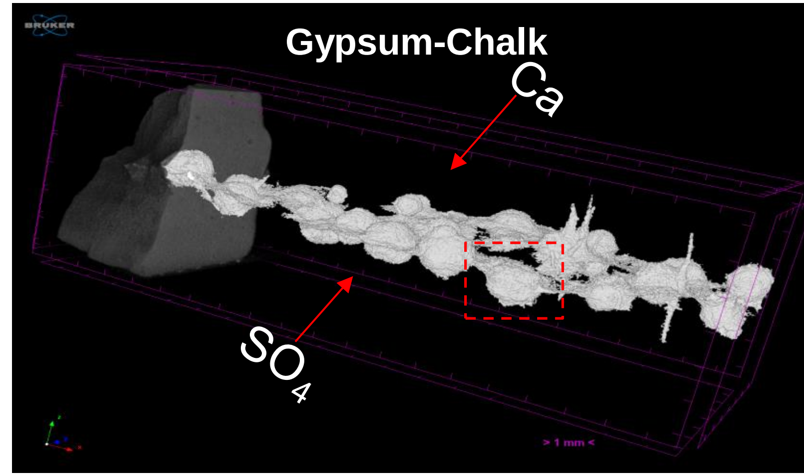


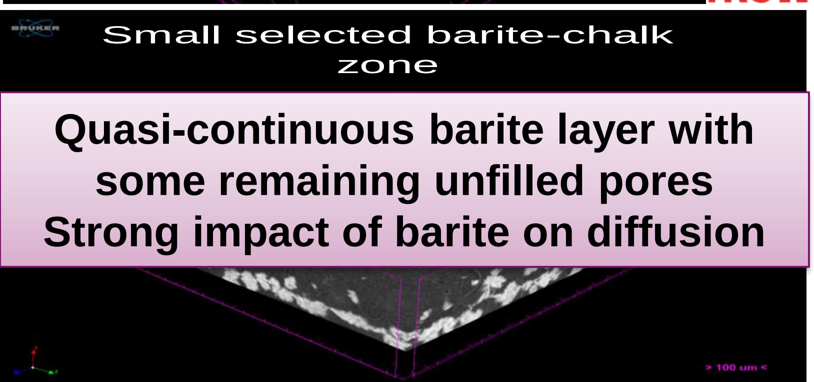


Code well reproduced the porosity reduction due to precipitation
Code under-estimated the precipitation impact on diffusion

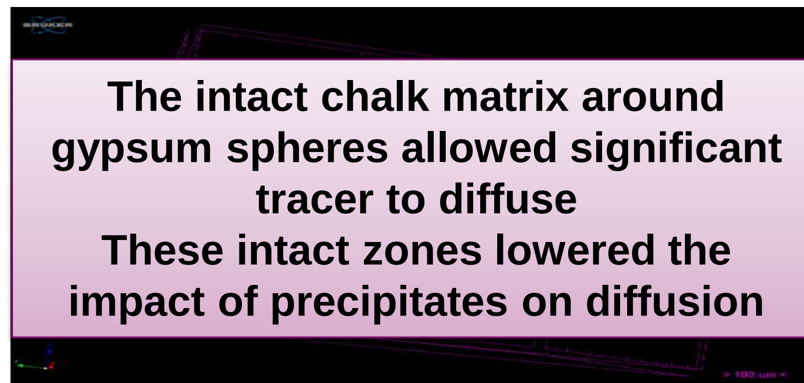
RESULTS: BARITE & GYPSUM EVOLUTION IN CHALK



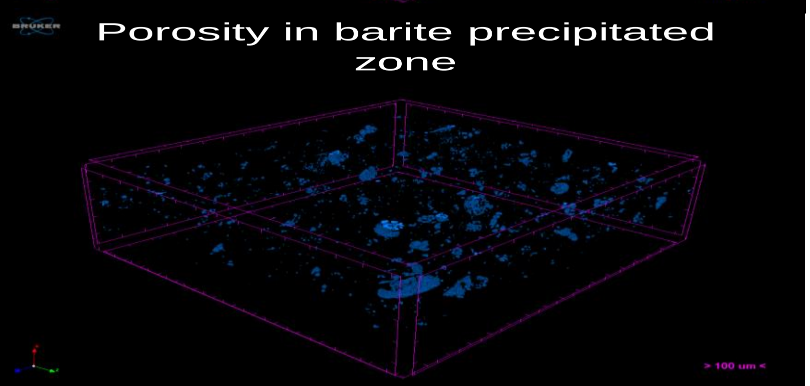


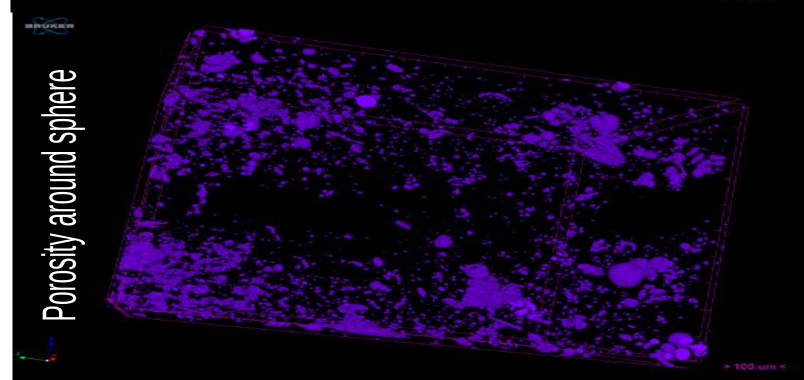


Quasi-continuous barite layer with some remaining unfilled pores
Strong impact of barite on diffusion

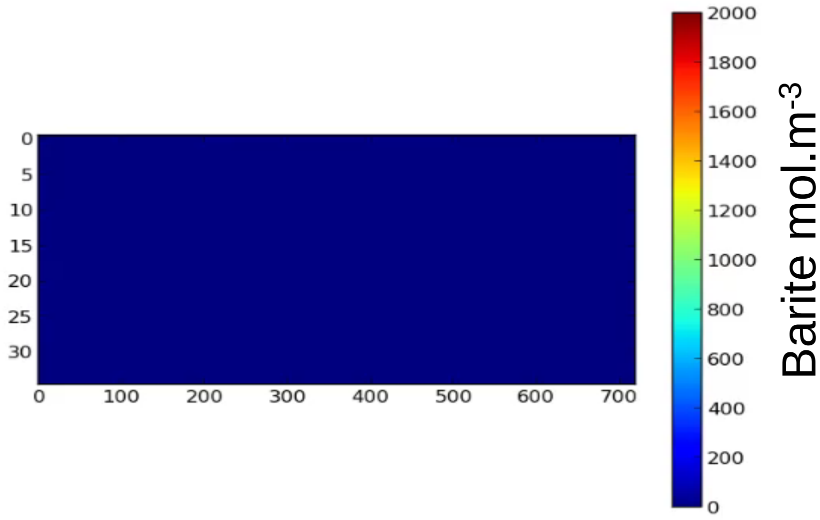


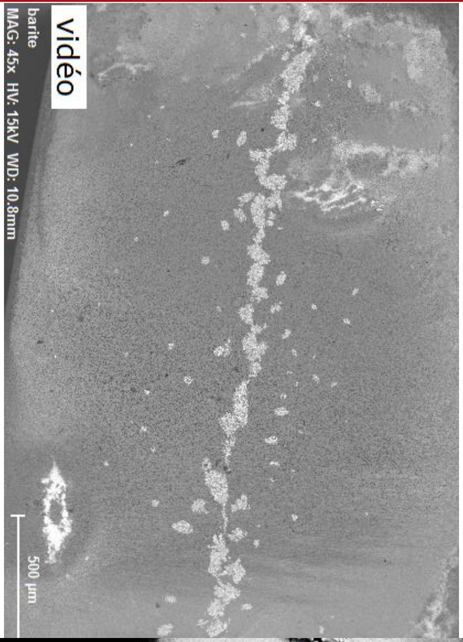
The intact chalk matrix around gypsum spheres allowed significant tracer to diffuse
These intact zones lowered the impact of precipitates on diffusion

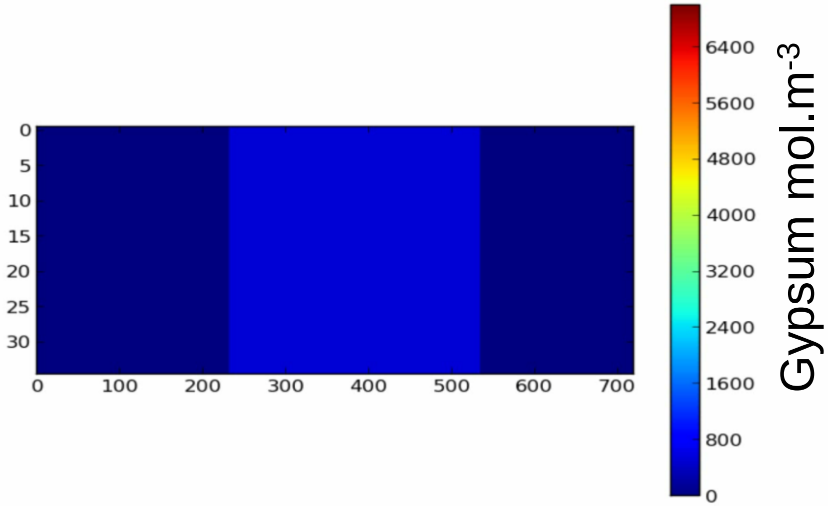


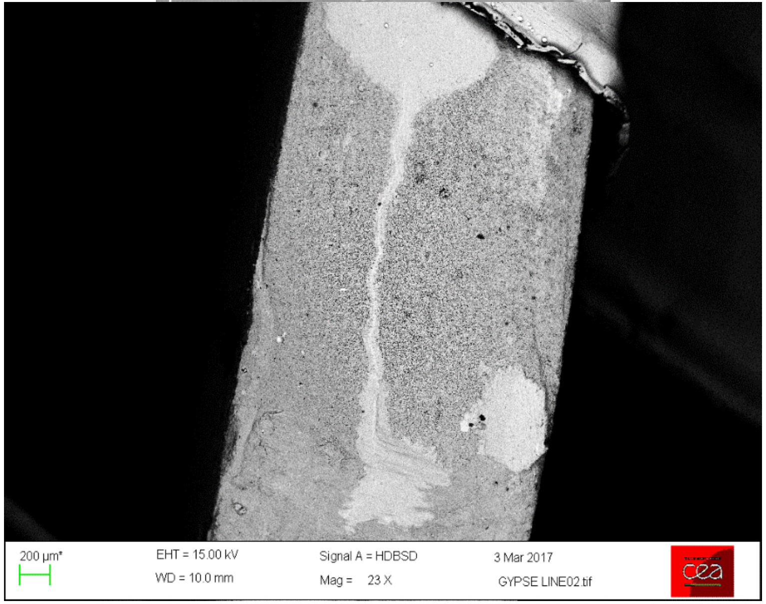


DISCUSSION: WHAT IS THE IMPACT OF SPATIAL VARIABILITY ON EVOLUTION OF MINERALS?









CONCLUSION

1. Can Empirical Archie's law reproduce mineral perturbation impact on diffusivity for a micritic chalk system?

➔ Code properly reproduced macroscopic precipitation impact on chalk porosity

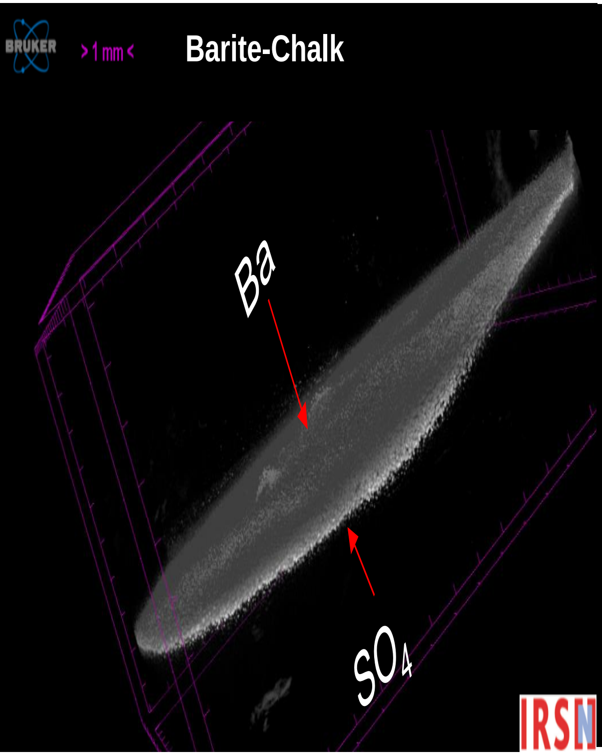
➔ Archie's law underestimated the impact on diffusivity

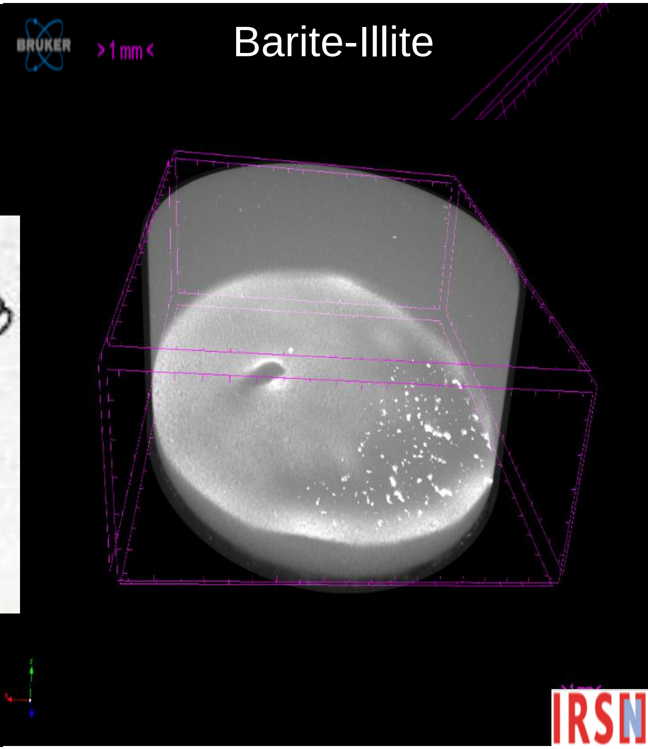
2. What is the impact of spatial variability on studied mineral perturbation and subsequently on diffusivity of water tracers?

➔ No significant impact on evolution of barite

➔ Significant impact on gypsum evolution ⇔ Isolated spheres = lower impact on diffusion

CLAY RESULTS





Please join me at my defense in october

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Thank you for your kind attention

Publication

S. Savoye, A. Rajyaguru, N. Macé, .S. Lefèvre, G. Spir, J.C. Robinet. How mobile is tritiated water through unsaturated cement-based materials? New insights from two complementary approaches, *Applied Radiation and Isotopes* 2018 139, 98-106.

Publication under revision

A. Rajyaguru, E. L'Hopital, S. Savoye, C. Wittebroodt, O. Bildstein, P. Arnoux, V. Detilleux, I. Fatnassi, P. Gouze, V. Lagneau. Experimental characterization of coupled diffusion reaction mechanisms in low-permeability rocks: A case of two extremities of sulfate alkali minerals. Submitted to *Chemical Geology* the 15th of May 2018

Publication Under preparation

A. Rajyaguru, S. Savoye, C. Wittebroodt , E. L'Hopital, V. Detilleux, V. Lagneau: Barite precipitation in compacted illite & kaolinite: evidence of surface charge on new formed mineral, for *Environment Science & Technology*

A. Rajyaguru, O. Bildstein, S. Savoye, C. Wittebroodt, P. Arnoux, V. Detilleux, V.Lagneau: Numerical characterization of coupled diffusion reaction mechanisms in low-permeable micritic chalk, for *Computers & Geosciences*

International Conference

Oral presentation at the Goldschmidt conference in August 2017, Paris

A. Rajyaguru, S. Savoye, O. Bildstein, C. Wittebroodt, V. Detilleux, P. Arnoux, V. Lagneau: An experimental vs. numerical approach to determine capability of Archie's law to explain impact of evolving porosity on diffusivity

International Workshop

Reactive Transport in the Earth and Environmental Sciences in the 21st Century, October 2017, Amboise, France

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