

# Matrix diffusion at the small scale and the role of heterogeneity

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# Outline

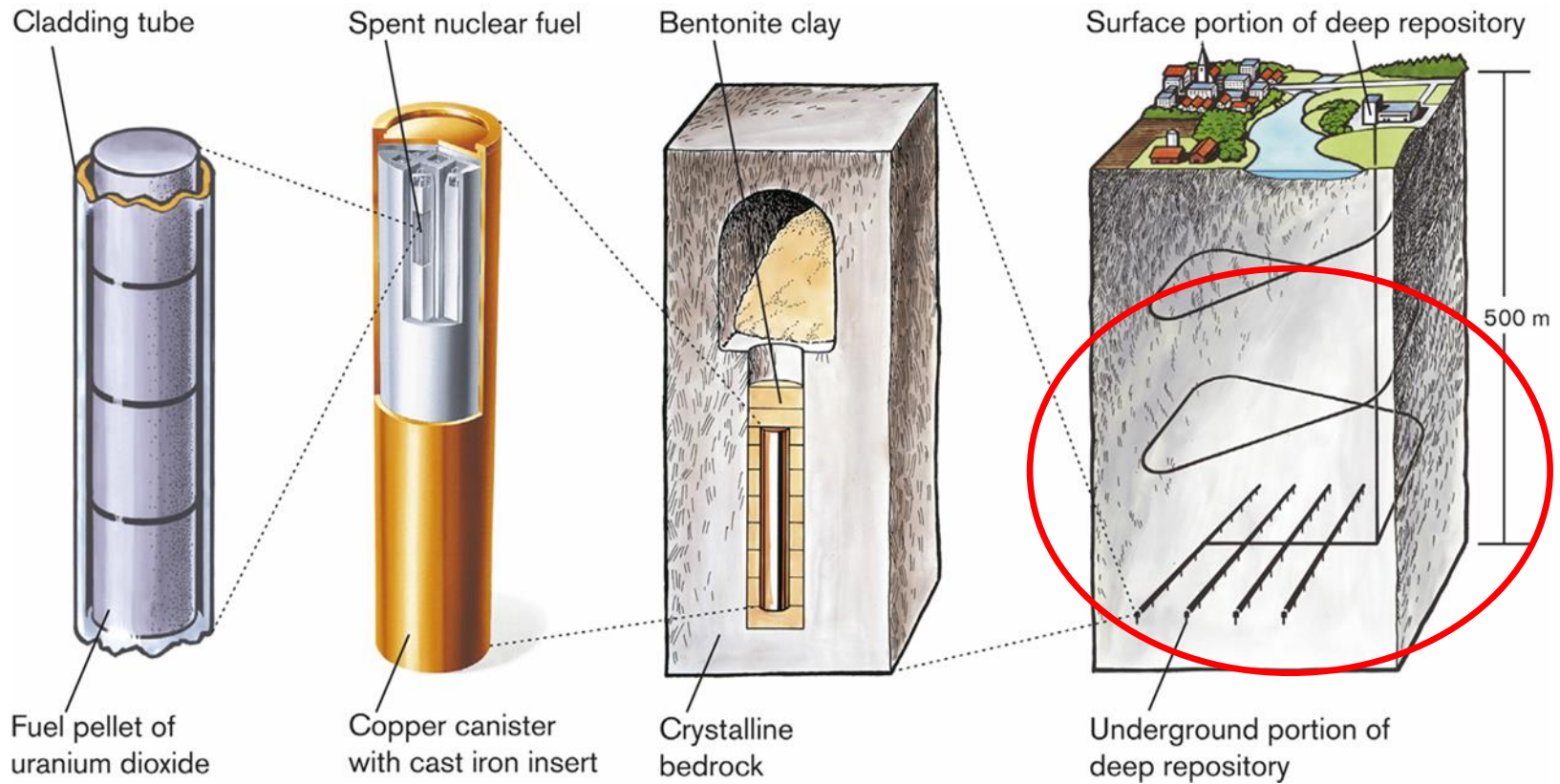
- Background
- C-14 PMMA autoradiography for structure characterization
- Diffusion studies -Outleaching of MMA
- TDD+TDRW modelling
- Permeabilities & Diffusivities & Geometry factors
- Uranium migration and fixation in a weathering profile in a granitic rock
- Conclusions



**Diffusion processes within crystalline rock :  
from petrography and matrix characterization to diffusion coefficients**



# Spent nuclear fuel repository KBS-3V concept





# Migration of radionuclides in fractured crystalline rock

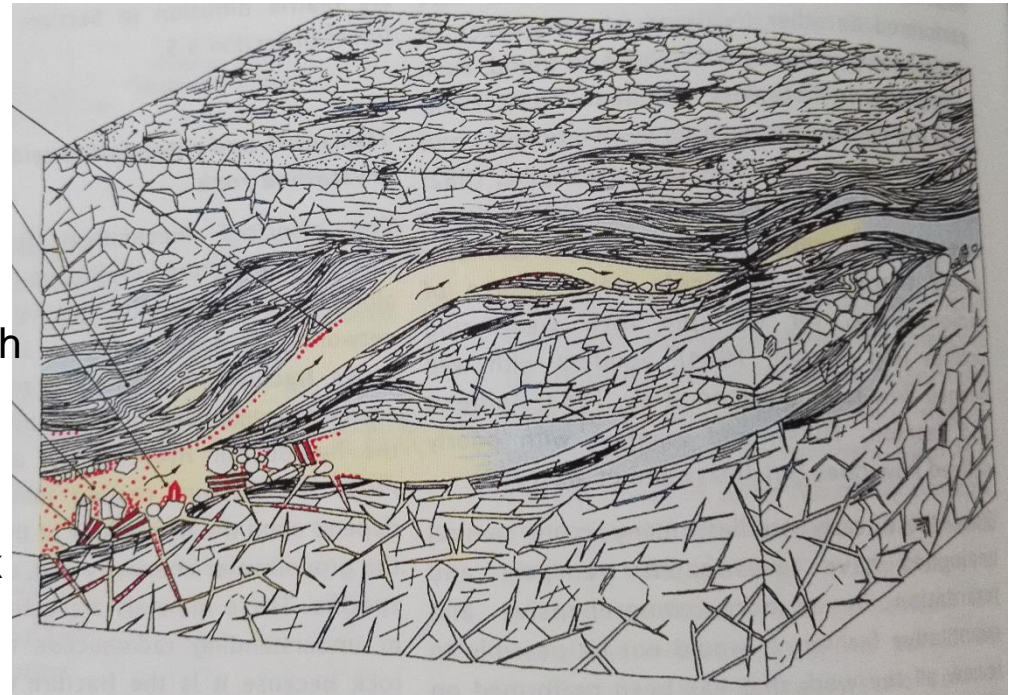
Sorption on the surface of the flow path

Precipitation

Advection /dispersion in the flow path

Diffusion and sorption in micropores

Diffusion into open pores of the rock matrix



*Modified from Miller et al. Geological disposal of radioactive wastes and natural analogues, Waste management series Volume 2, 2000*



## Mathematics for solutes transport in fractures

$$C_f(L, t) = C_o \operatorname{erfc} \left( ut^{-1/2} \right)$$

$$u = \sqrt{\varepsilon_p D_e R_p} \frac{WL}{Q}$$

$$R_p = 1 + \frac{1 - \varepsilon_p}{\varepsilon_p} K_d \rho_s$$



## Effective diffusion coefficient, porosity, distribution coefficient

$$D_e \quad K_d$$

$$D_e = D_p \cdot \varepsilon_p = D_w \cdot G \cdot \varepsilon_p = D_w \cdot G_f$$

$$D_a = D_p \cdot R^{-1} = D_e \cdot \varepsilon_p^{-1} \cdot R^{-1} = D_e \cdot \alpha^{-1}$$

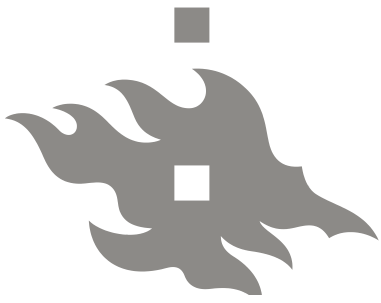


# C-14 PMMA autoradiography for **connected porosity** and structure characterization

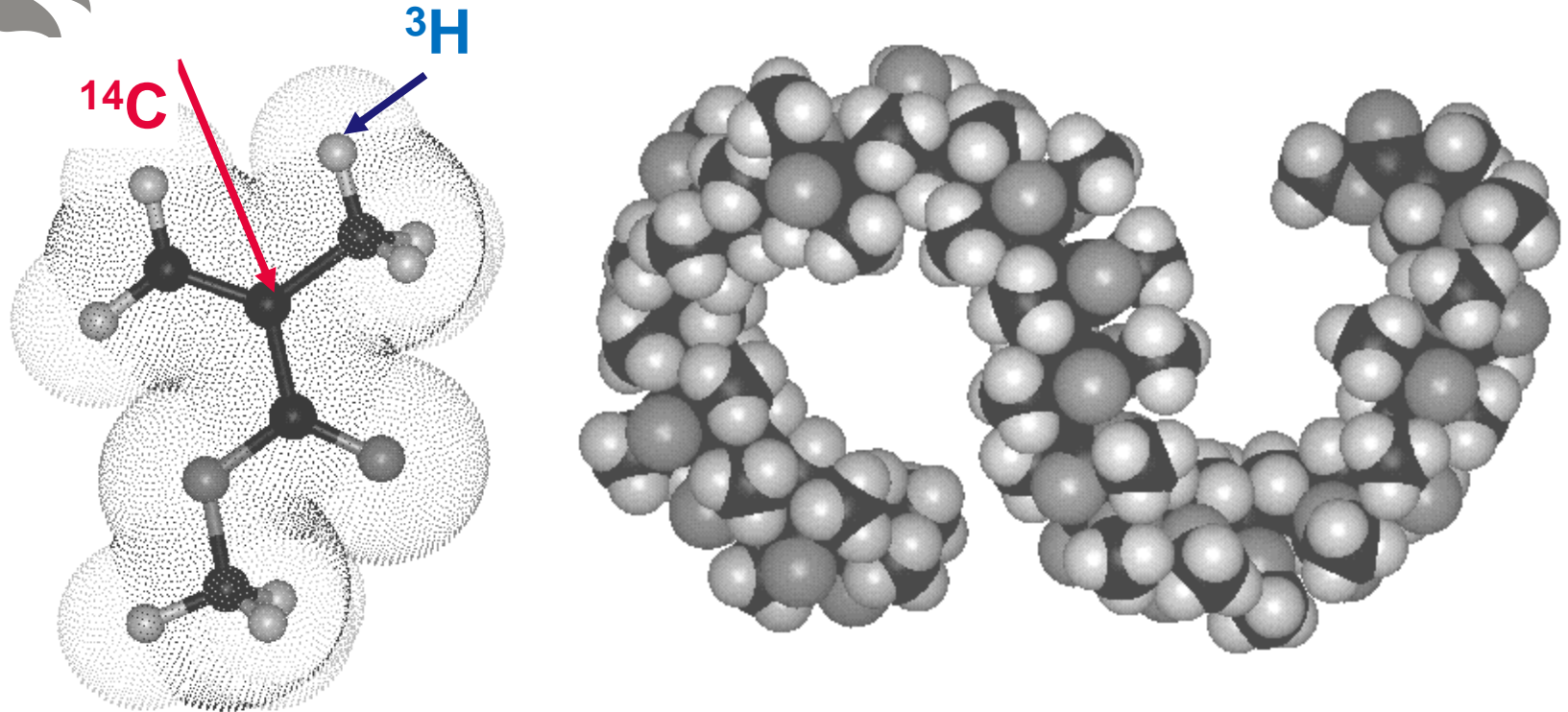
- Drying of rock core samples
- Impregnation of rock core samples with C-14 labelled METHYLMETHACRYLATE in vacuum
- Polymerisation of MMA into PMMA
- Autoradiography of sawn and polished rock surfaces
- Digital image processing of autoradiographs
- **Final result : Multiscale and Quantitative mapping of rock porosity!**

*J Sammaljärvi et al (2012) Free radical polymerisation of MMA with thermal initiator in brick and Grimsel granodiorite in Engineering Geology 135-136, 52-59*





# Methylmethacrylate molecule



The low molecular weight and low viscosity carrier monomer MMA, which can be fixed after impregnation by polymerisation. When labelled with radioactive  $^{14}\text{C}$  or  $^3\text{H}$  which have low beta energies (155 keV and 18 keV respectively) autoradiography method can be used to describe the spatial distribution of the porosity.



# Autoradiography



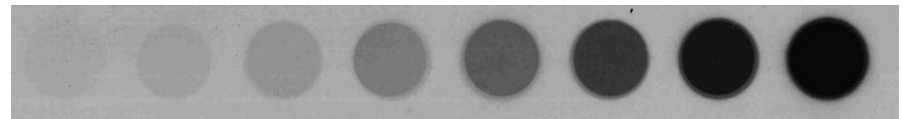
14 cm

Photograph of the sawn rock surface

C-14-PMMA Standards



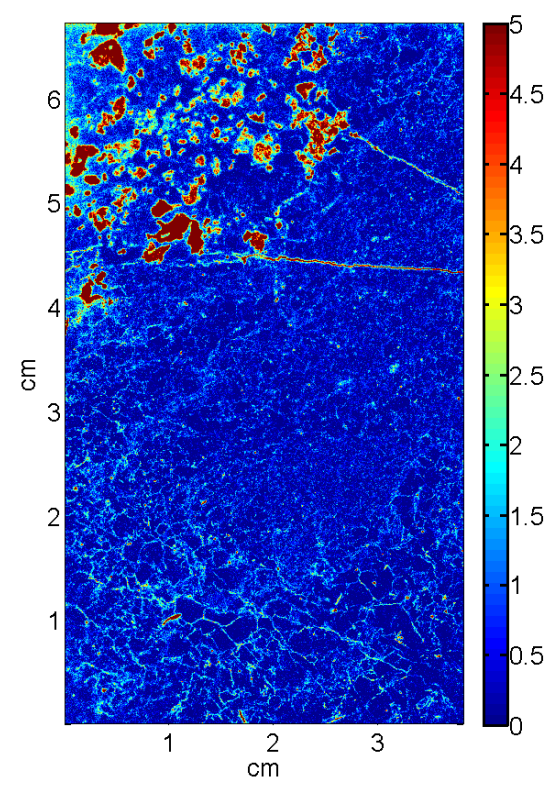
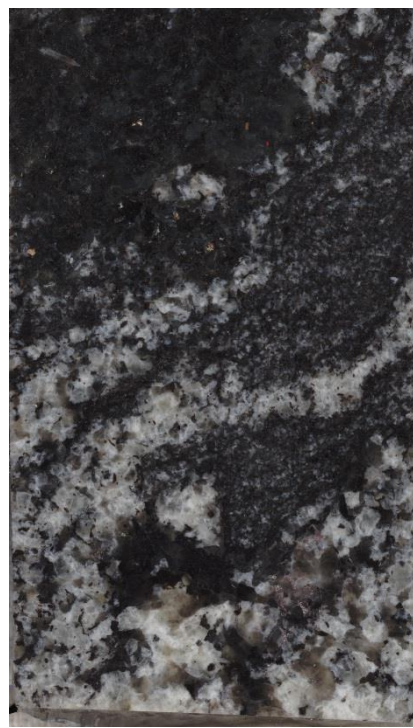
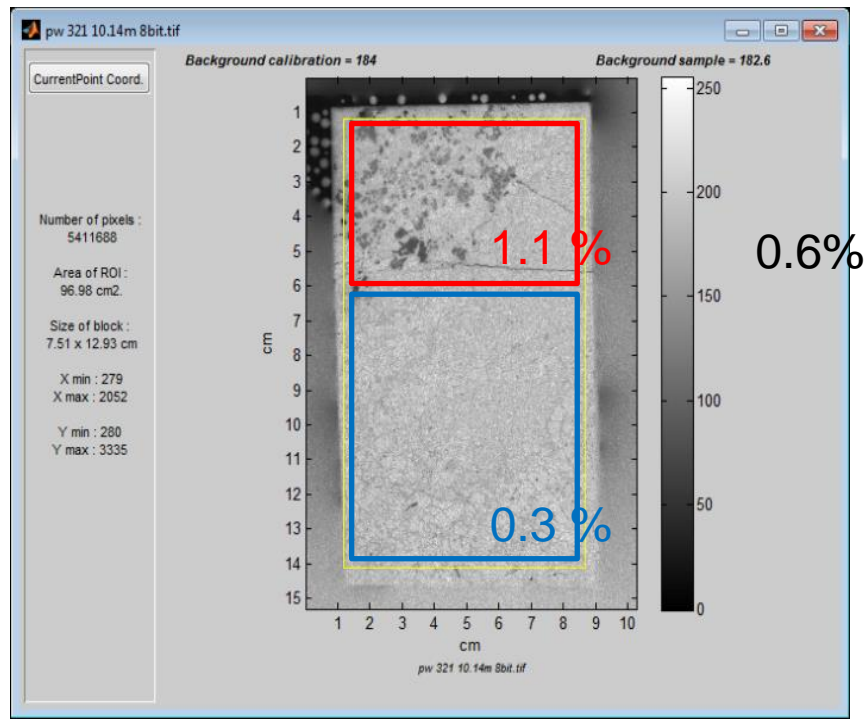
C-14-PMMA autoradiograph



From 0.46 kBq/ml to 92.5 kBq/ml

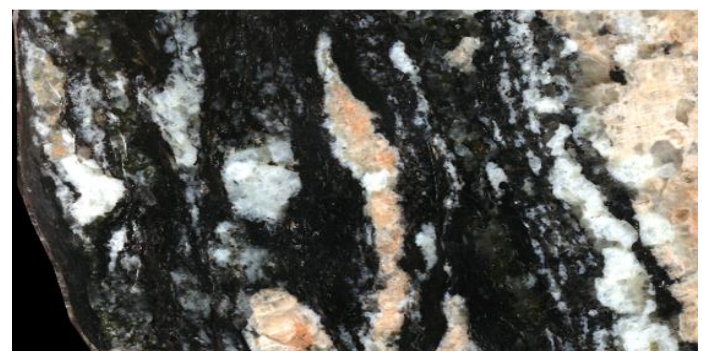
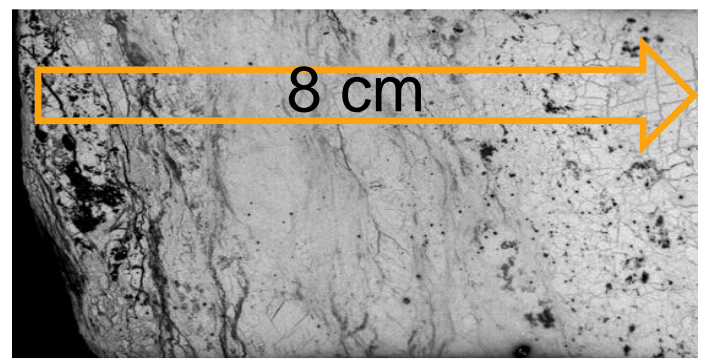
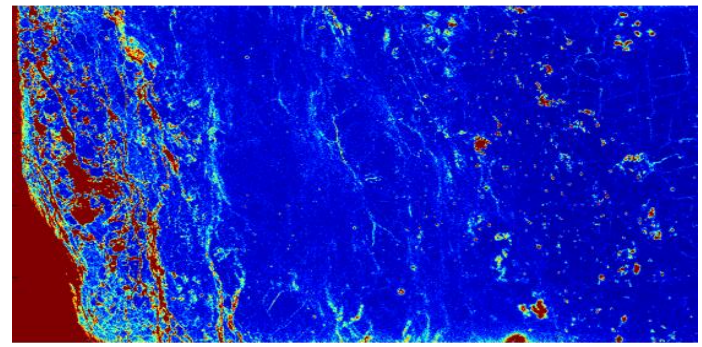
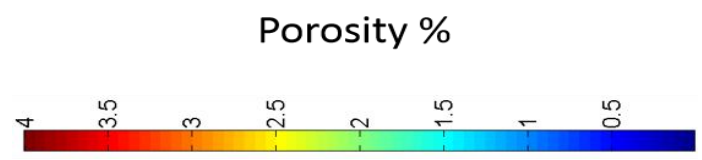
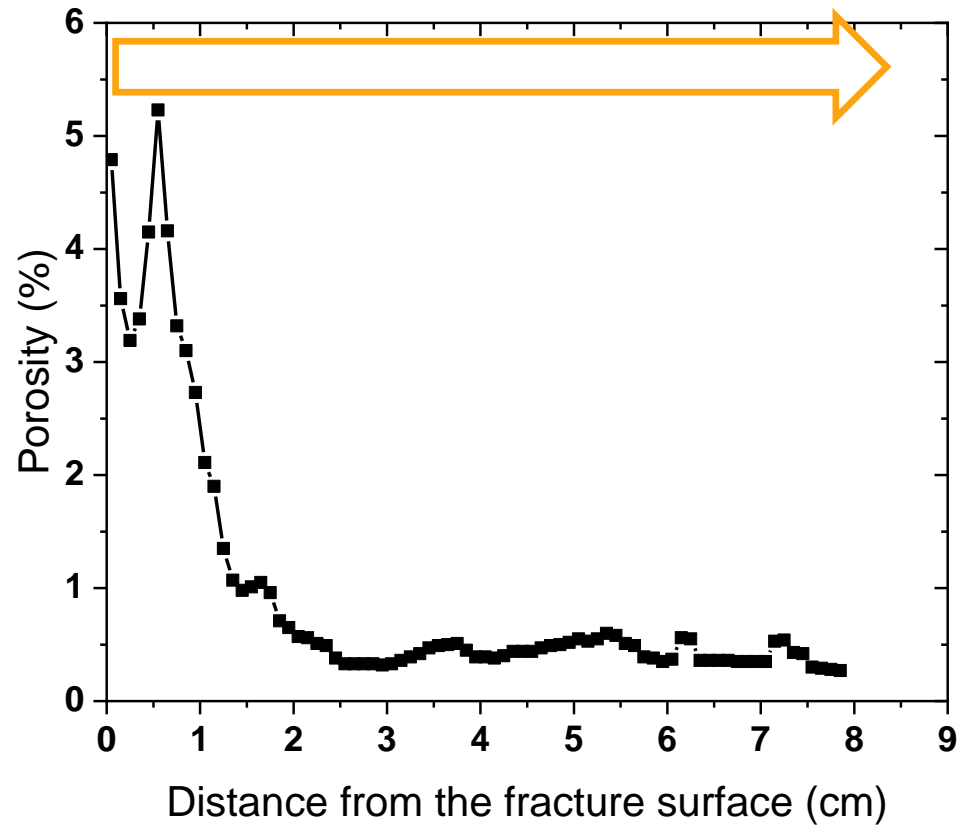


# The amount of C-14-PMMA in the rock sample is converted to a porosity map





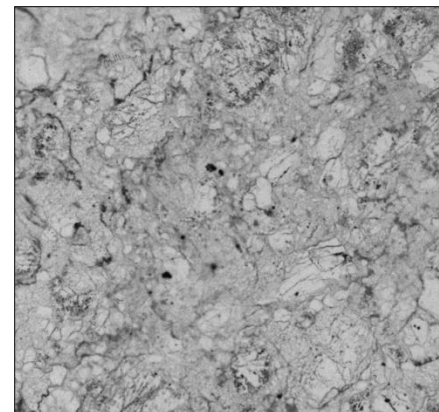
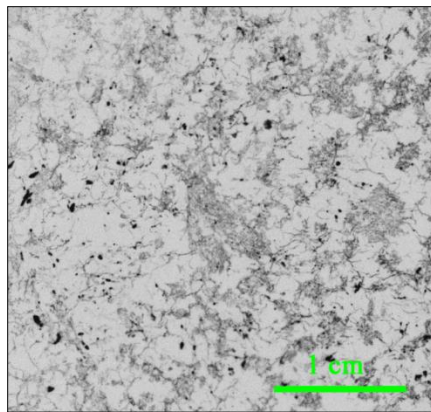
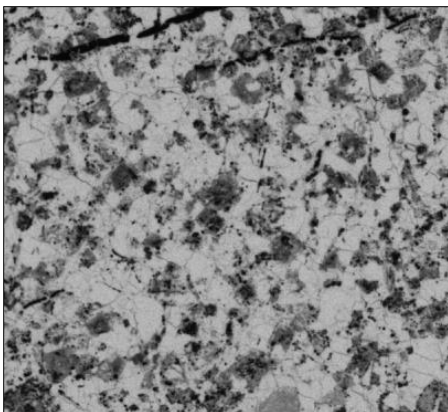
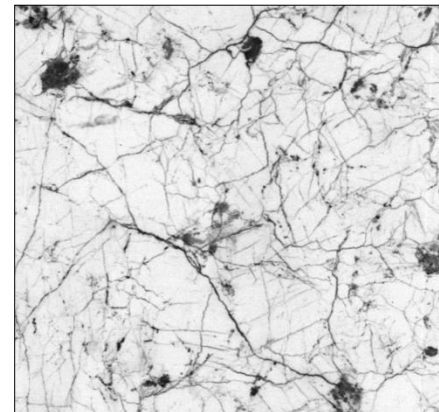
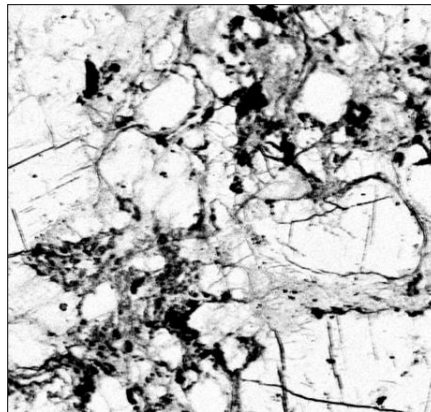
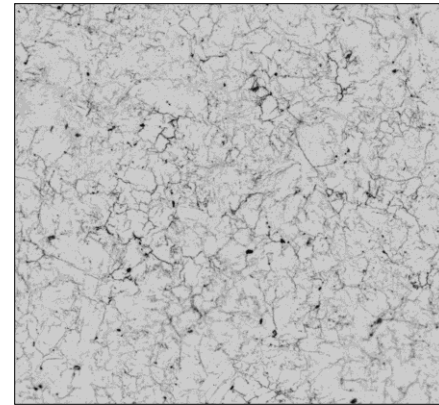
# Porosity profile





# Pore space description of crystalline rocks

		1	1 : Charroux tonalite
	2	3	2 : Kivetty granodiorite
4	5	6	3 : Palmottu granite
			4 : Le Bourneix granite
			5 : Charroux monzodiorite
			6 : Grimsel granodiorite

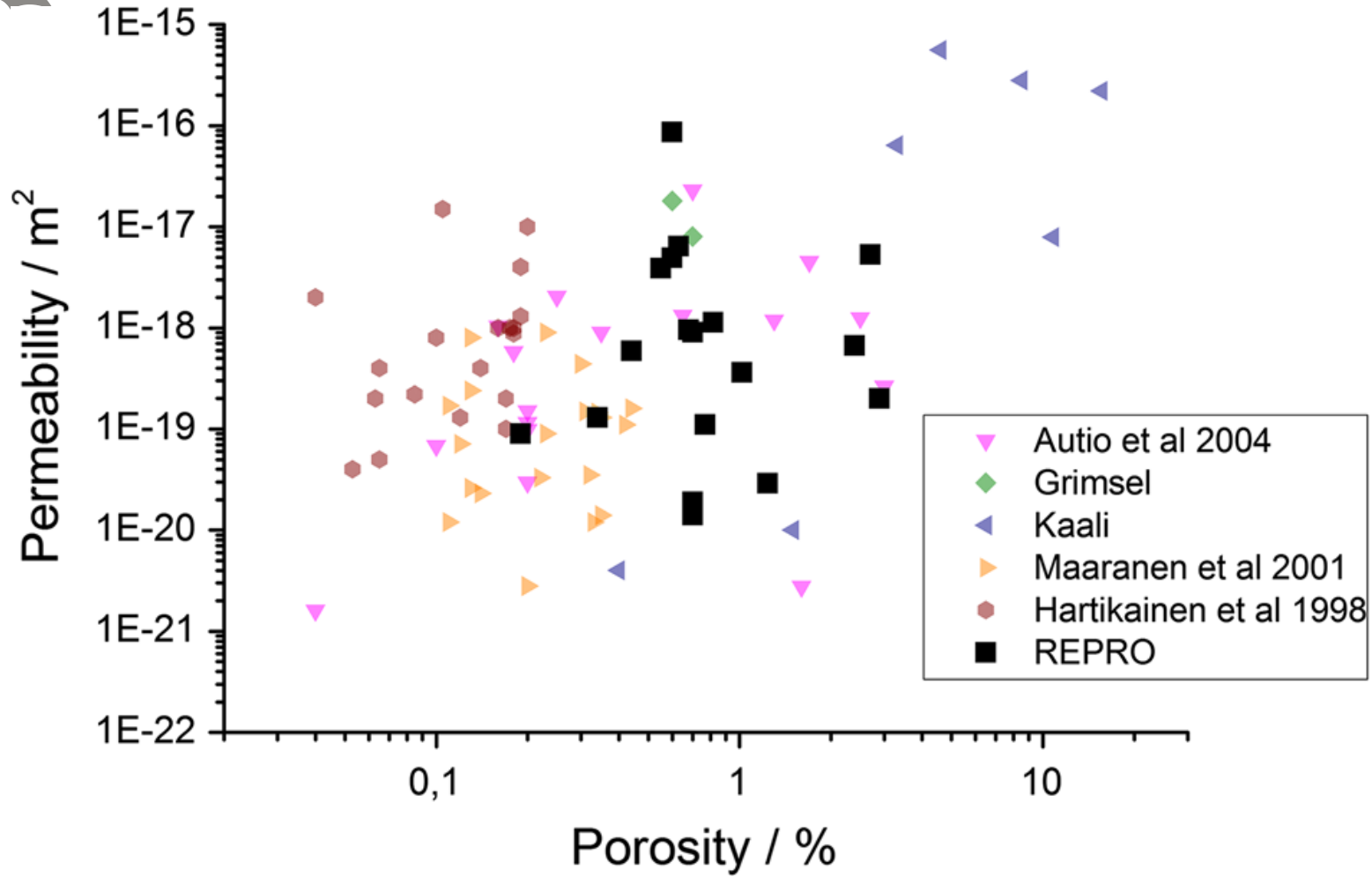


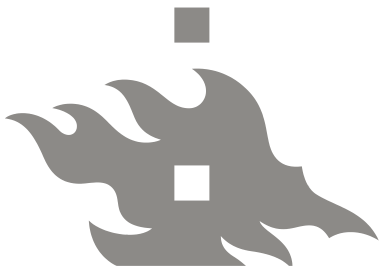
■ Porous patches

+

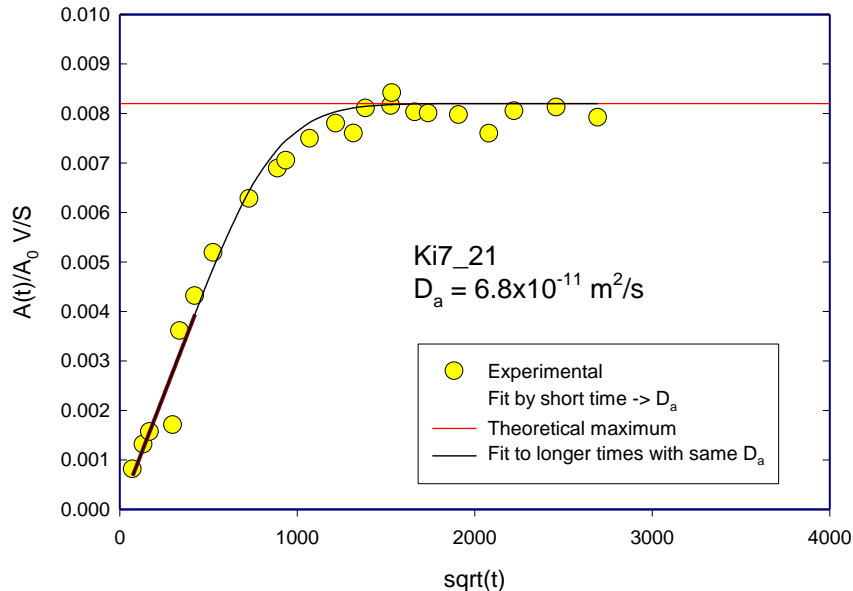
Microcracks

# Permeability versus porosity by He gas method

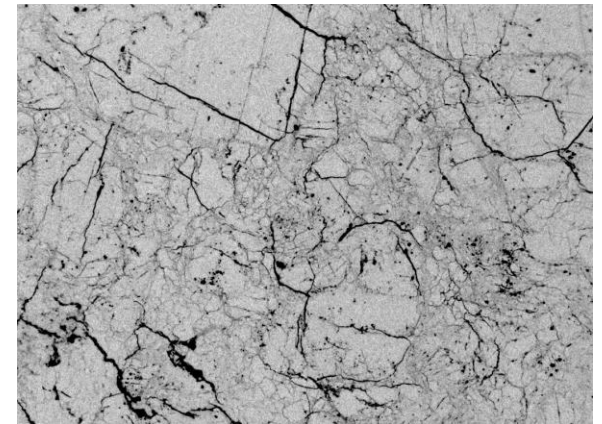




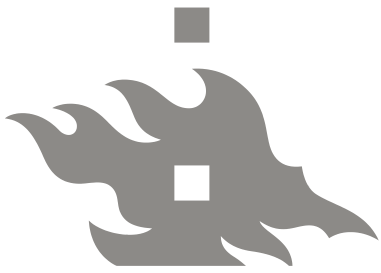
# How to explain heterogeneous diffusion by homogeneous models?



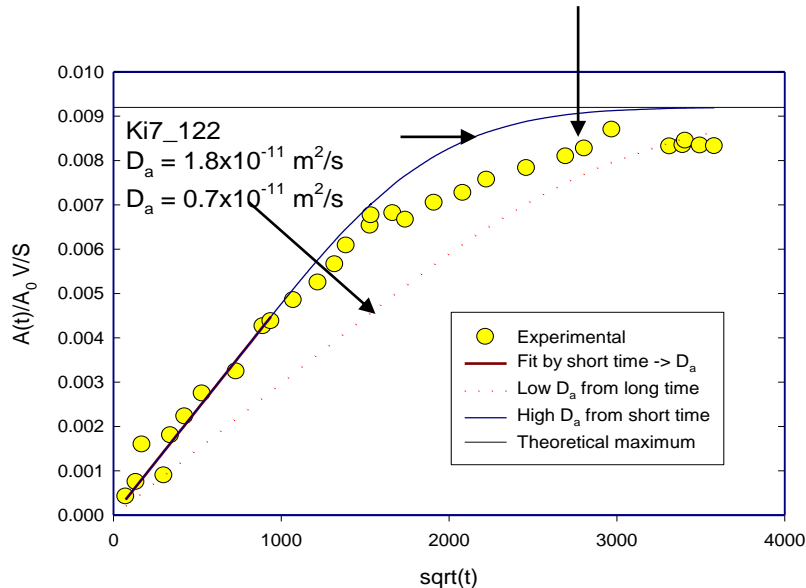
5 cm



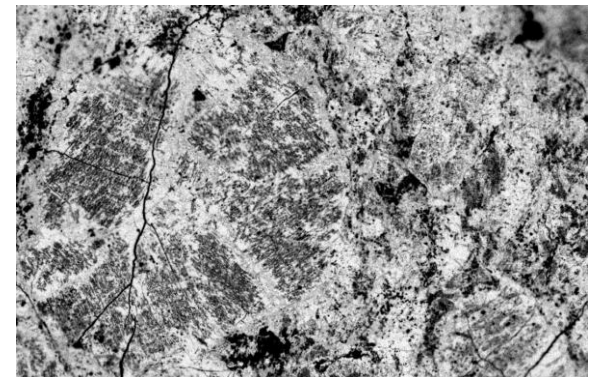
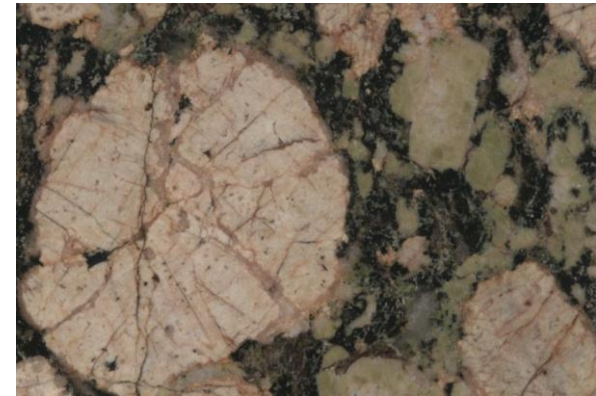
Outleaching of  $^{14}\text{C}$ -MMA from the rock core  
Kivetty, unaltered porphyritic granodiorite  
-intermediate and acidic plutonic rock  
-porosity of 0.3 %  
-diffusion occurs mainly along fissures



# How to explain heterogeneous diffusion by homogeneous models?



5 cm



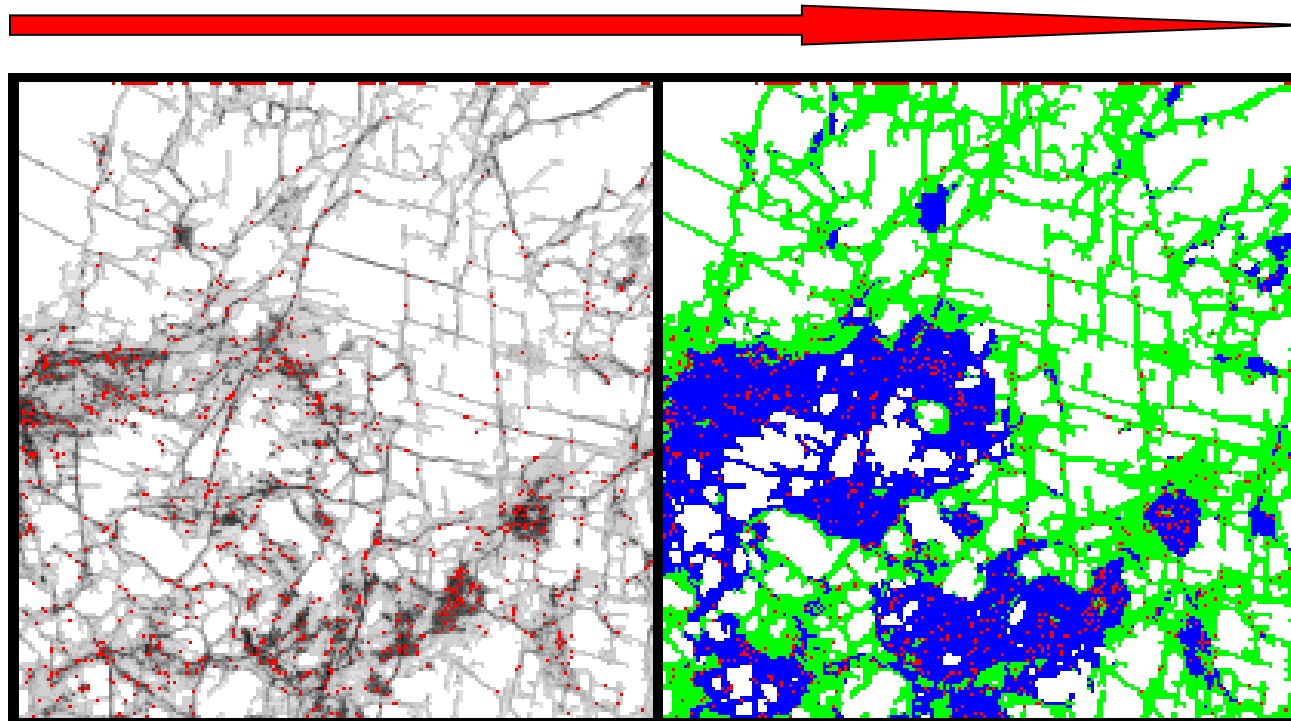
Outleaching of  $^{14}\text{C}$ -MMA from the rock core Kivetty, altered porphyritic granodiorite  
 -Plagioclase to serisite, biotite to chlorite  
 -porosity of 1.2 %  
 -due to alteration complexity of the structure increases, two-phase diffusion found



# Solute transport in fractured media

Interpretation of diffusion experiments on crystalline rocks using random walk methods: Time domain diffusion modelling

Flow in a fracture



Matrix diffusion/sorption

3 cm

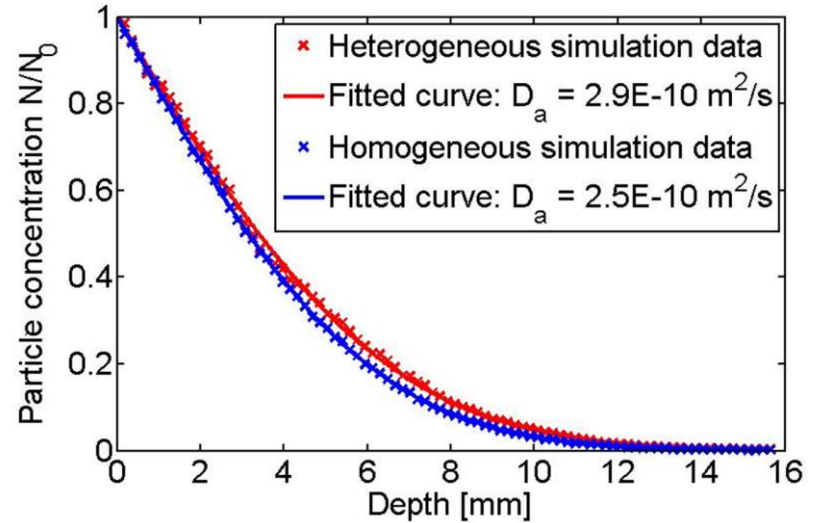
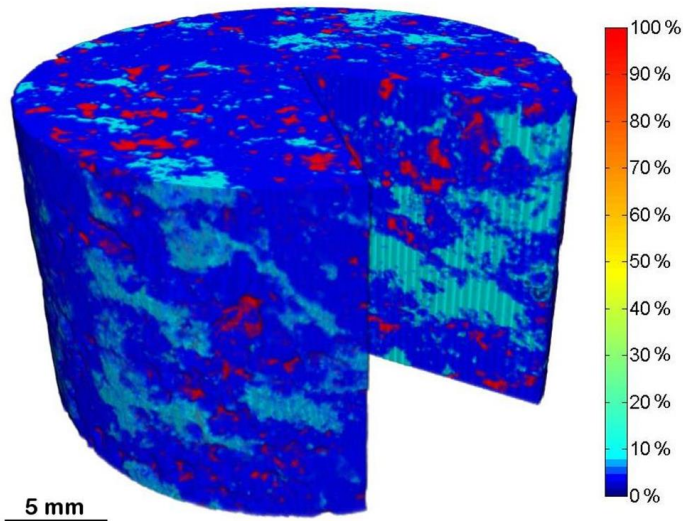
PMMA Autoradiograph

Porous subset

# Altered Sievi tonalite, Finland

## PMMA mineral specific porosity + CT tomography

## HTO through diffusion + TDD modelling



Left: Three dimensional porosity map of a sample of Sievi tonalite generated by applying  $^{14}\text{C}$ -PMMA method, mineral staining and X-ray microtomography. Altered feldspar appears blue (porosity 4.5%), altered mica light blue (8.6%), and large pores red (100%). Total porosity of 9%.

Right: In-diffusion profiles simulated by TDD in Sievi tonalite assuming a heterogeneous (red) and homogeneous (blue) porosity in the rock matrix.

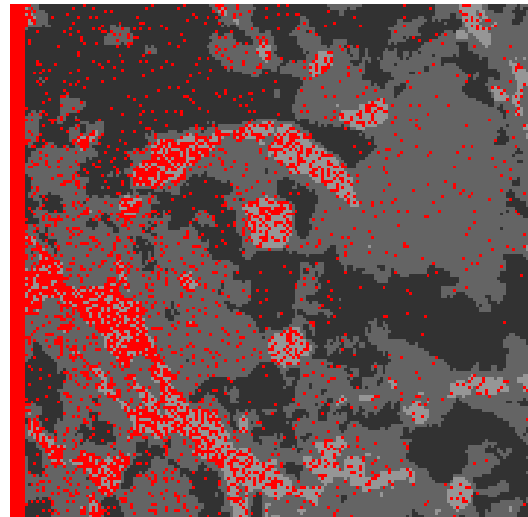
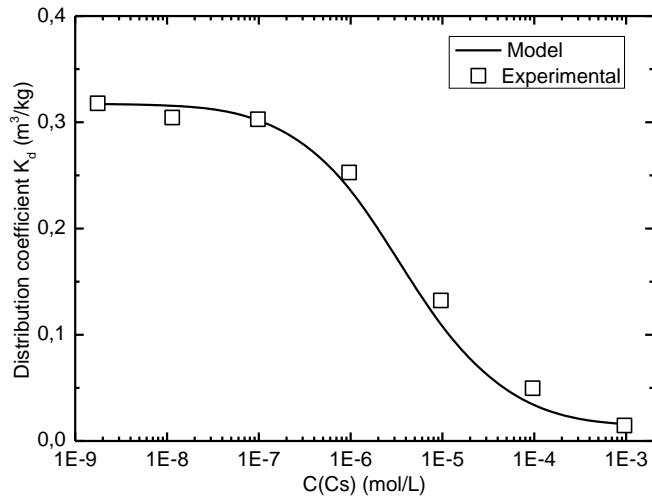


# Grimsel granodiorite

## Cs in diffusion + PMMA mineral specific porosity + CT tomography + mineral specific sorption (batch) + TDD modelling

Behavior of Cs in Grimsel granodiorite Part I: Sorption on main minerals and crushed rock (PhreeqC modelling)

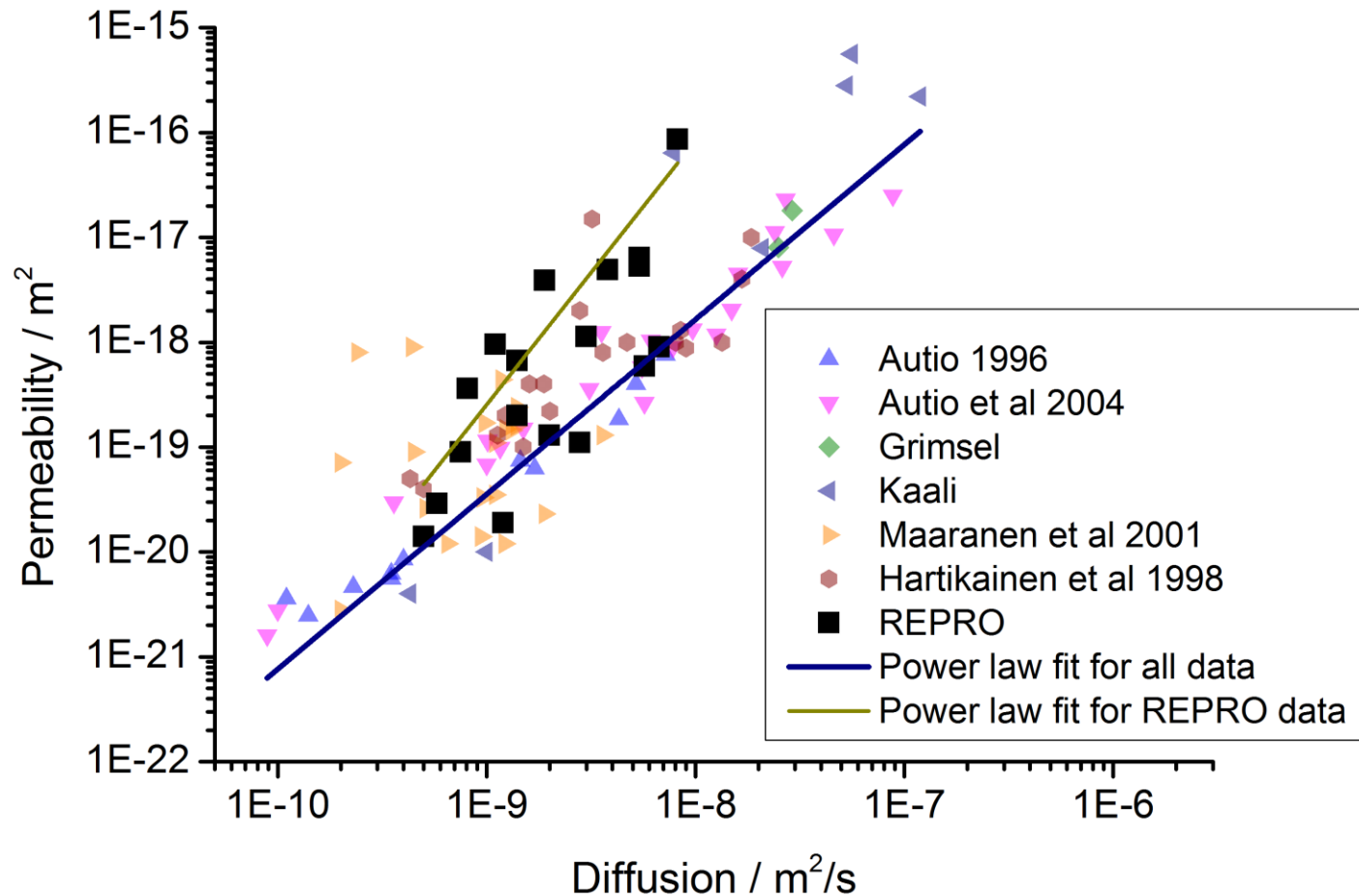
Behavior of Cs in Grimsel granodiorite Part II: Simulated diffusion in heterogeneous structure



*M Voutilainen et al (2017) Modeling transport of cesium in Grimsel granodiorite with micrometer scale heterogeneities and dynamic update of  $K_d$ , Water Resources Research 53, 9245-9265. [10.1002/2017WR020695](https://doi.org/10.1002/2017WR020695)*



# Permeability versus diffusivity by He gas method





# Geometry factor Archie's Law

Parkhomenko 1967 found a statistical correlation between the formation factor and the porosity:

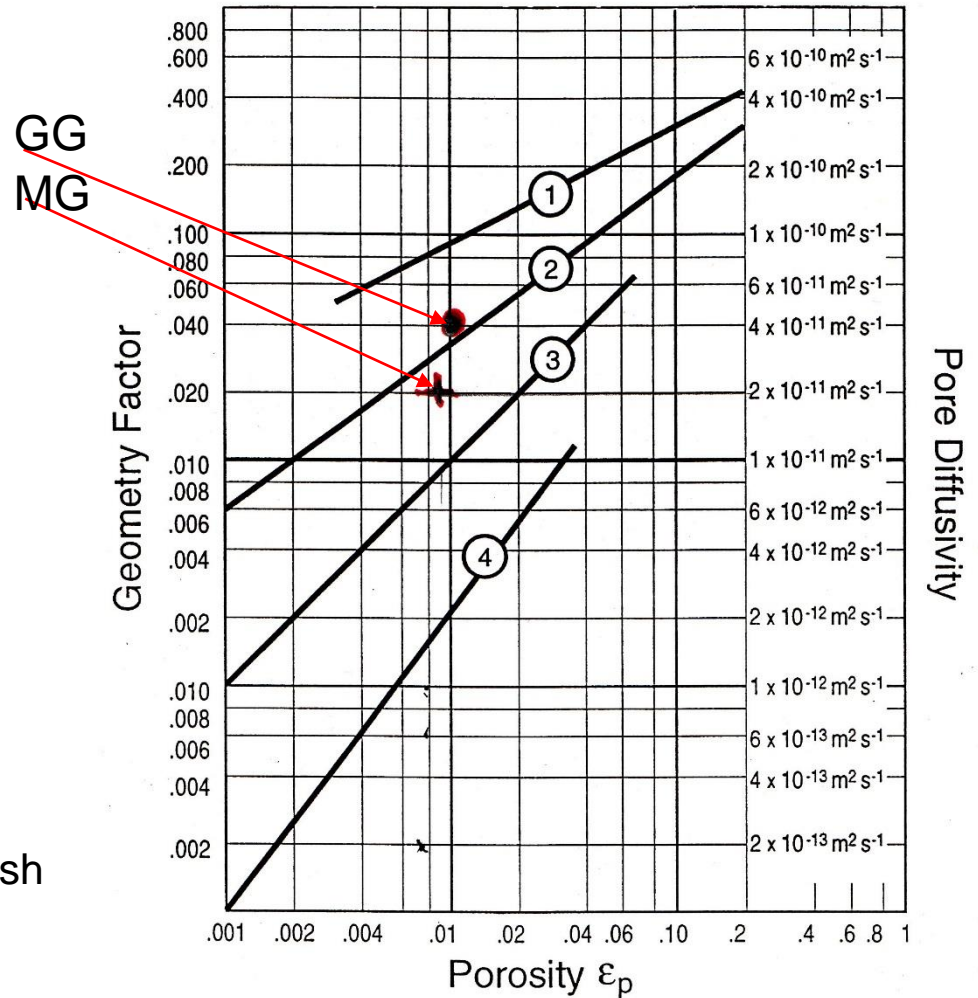
$$G_F = 0.71 \cdot \varepsilon_p^{1.58}$$

$$G_F = G \cdot \varepsilon_p$$

giving the geometry factor :

$$G = 0.71 \cdot \varepsilon_p^{0.58}$$

1. Fresh granites, brittle deformation
2. Fresh granites, fracture breccias
3. Granites with argillaceous alteration, fresh gneisses
4. Gneisses, with argillaceous alteration



*U Frick, (1992) An evaluation of diffusion in the groundwater of crystalline rocks Interner Berict 92-92E*

# Uranium migration and fixation in a weathering profile in granitic rock

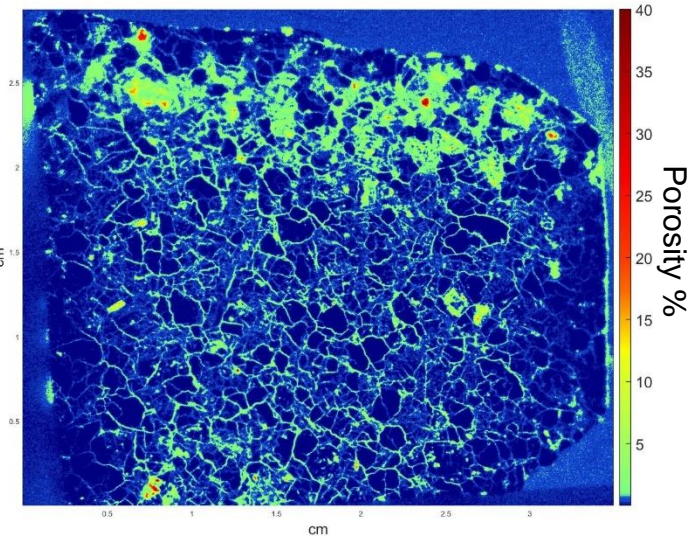
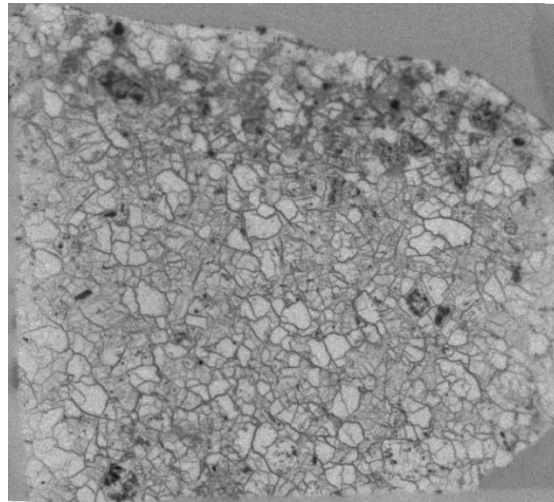
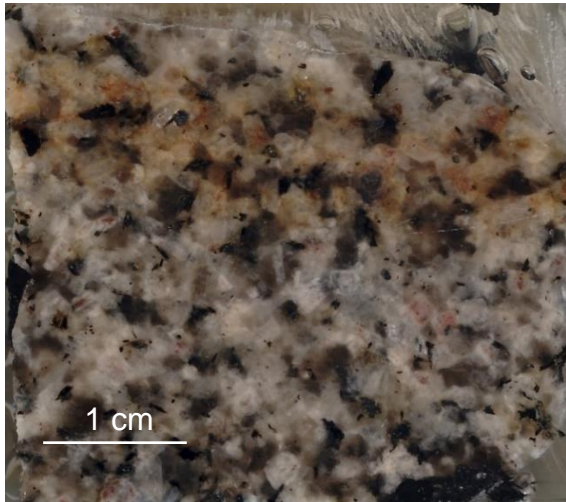


- The weathering profile of postglacial age (10000-15000 a) in a muscovite granite boulder sample.
- Stable isotope studies  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  to confirm that mineralogical changes are due to old hydrothermal events.
- The profile was evaluated with the aid of uranium content and uranium series isotope data.
- The connected porosity and pore structure were analyzed by C-14 PMMA autoradiography.
- The effective diffusion coefficients were measured via through-diffusion of HTO and  $\text{Cl-36}$  and with helium gas diffusion method.
- Fission track and electron microscopy with energy dispersive spectroscopy were used to analyze the uranium phases in detail.

Marcos et al.(2001) Discussion on the use of matrix diffusion model after a multidisciplinary study of a granitic boulder sample, In: K. P. Hart and G. R. Lumpkin (eds.), in *Scientific Basis for Nuclear Waste Management XXIV, Mater. Res. Soc. Symp. Proc.* 663, 1053-1063.



# Uranium in weathering profile in muscovite granite boulder (Hämeenlinna); C-14 PMMA porosity



The porosity values of feldspars within the altered zone varied between 3 and 7% whereas porosity values of feldspars in the fresh zone were 0.3 to 0.5%. Porosity values of quartz grains (0.05%) remain the same in both zones. Bulk porosity varied between 0.8 and 1.2% in the weathered zone and between 0.4 and 0.6% in the fresh zone.

*Lindberg et al. (1992). Effects of water-rock interaction on the porosity and composition of rock studied by impregnation with carbon-14-polymethylmethacrylate. In Water-rock interaction : Proceedings of the 7th international symposium on water-rock interaction - WRI-7, Park City, Utah, USA, 13 - 18 July 1992 (pp. 573-576 ). Y.K.Kharaka*



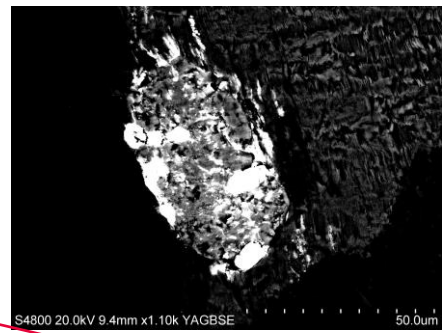
# Uranium in weathering profile in muscovite granite boulder (Hämeenlinna); relation to mineralogy and occurrence of Uranium



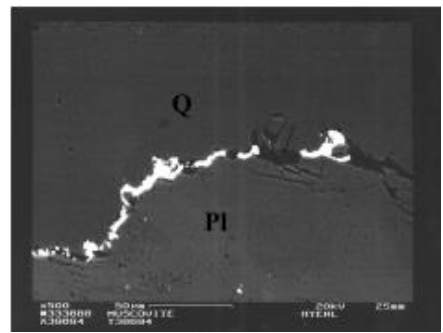
U occurrence by fission track method



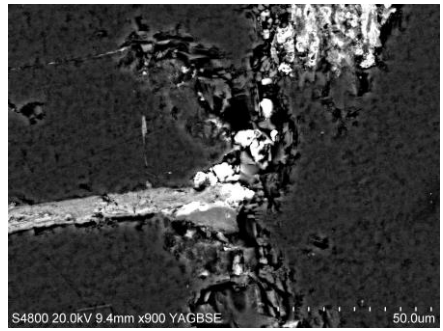
Thin section of MG



apatite +U



uranophane



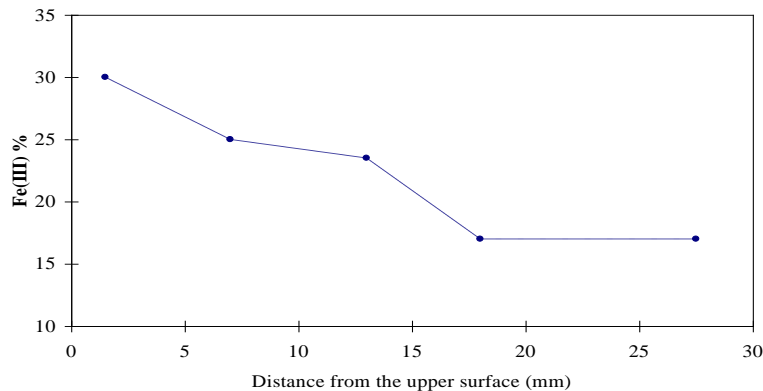
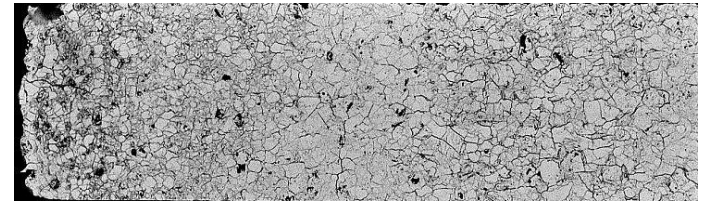
biotite +U

U occurrence by SEM/EDS

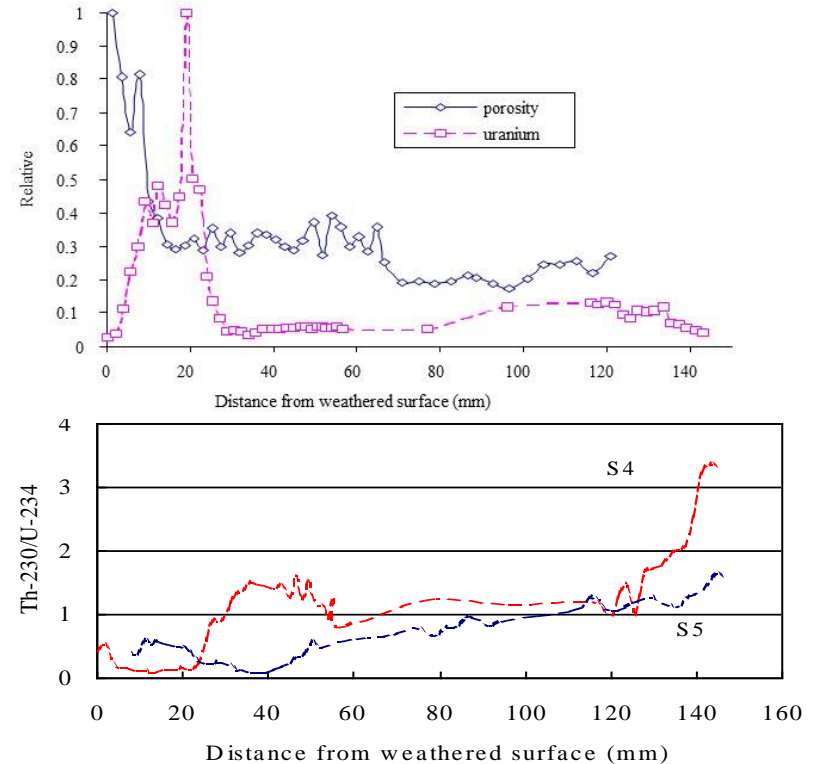


# Uranium content and the porosity in the weathered muscovite granite sample; relation to the Fe(III) decrease in the sample

The uranium distribution in the rock shows a strong uranium accumulation in the area of 15 to 22 mm from the rock surface at about ten mm beneath the edge of brownish area. The radioactive equilibrium in the uranium decay series is disturbed  $^{230}\text{Th}/^{234}\text{U}$  activity ratio indicates existing mobile uranium in the system.



Fe(III) content versus distance from the weathered surface. Mössbauer analyses from biotites shows Fe(III) content decrease from 25-30% within upper 12 mm down to 17% at 17-31 mm depth.





# Conclusions

- Since the early 1990's we have studied the pore network and related transport and storage properties of a large number of granitic rocks, mainly at repository candidate sites and natural analogue sites in Finland, as well as from foreign sites and underground research facilities.
- The results indicate that matrix diffusion is an important phenomenon and its extent depends on the connected pore structure of the host rock as well as on the mineral composition.
- There have been found no indications that processes at reaction fronts might have blocked pore networks completely; only rare cases of a decrease of transmissivity have been observed.
- The general observation from a large number of investigations was that hydrothermal alteration, which most often selectively affected plagioclase and biotite, always resulted in a significant increase in porosity, hydraulic conductivity and diffusivity.

# Realistic systems: geometries



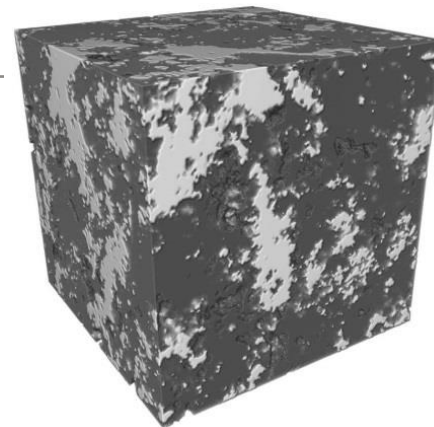
Rock sample



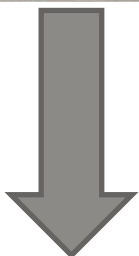
X-ray tomography

Digital 3D image

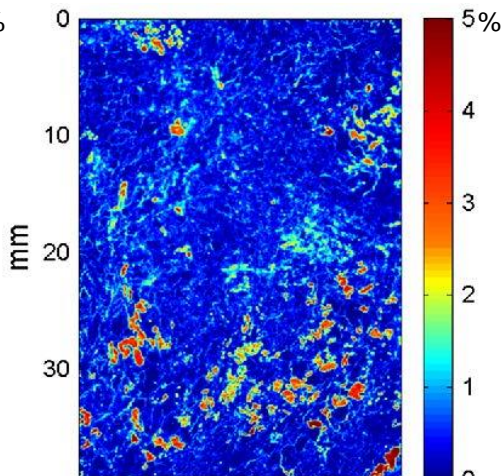
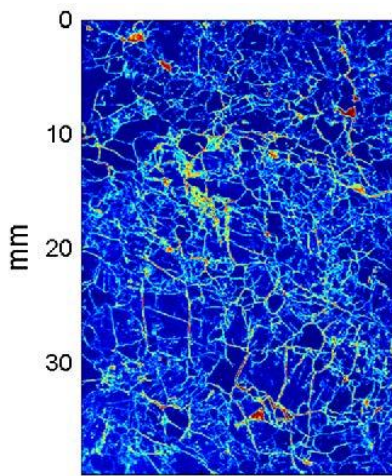
Fractures, 3D mineral distribution



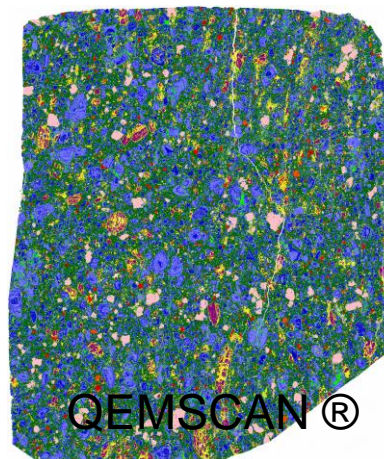
C-14-PMMA  
Autoradiography



Connected Microporosity, Digital 2D image



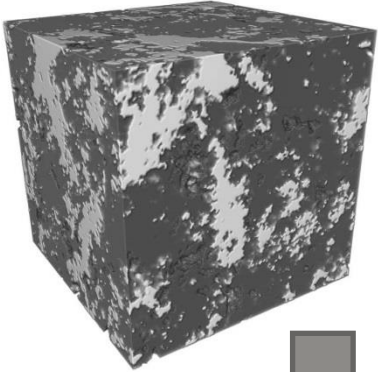
Mineral texture, pore apertures,  
and elemental composition



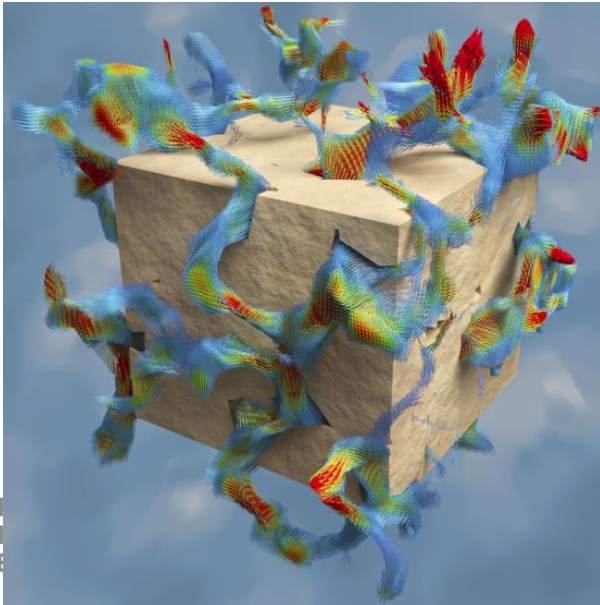
- Quartz
- Magnetite/Hematite
- Magnetite/Hematite + Ti
- Ilmenite
- Anorthite
- Bytownite
- Labradorite
- Andesine
- Oligoclase
- Hornblende
- Montmorillonite
- Kaolinite
- Zircon
- Other silicates
- Apatite
- Sulfide mineral
- Calcite
- Ankerite
- Siderite
- Dolomite
- Rhodocrosite
- Glass
- Gypsum
- Other mineral
- Non identified

# Realistic systems: modelling

Digital 3D image



Lattice-Boltzmann simulation



Flow field for advection

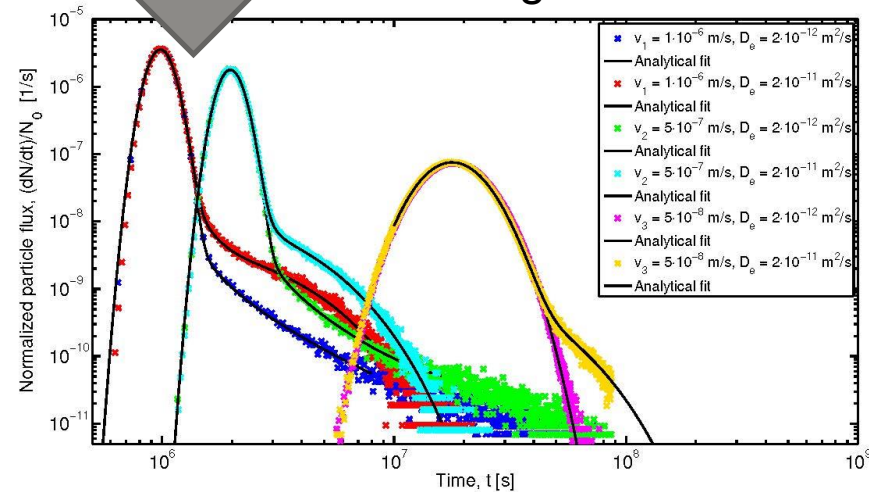
Realistic model

Time domain-Random walk simulations

Batch sorption experiments

Distribution coefficients for sorption

Breakthrough curves





Thank you!



RIP (Radionuclides in porous bedrock) team