Matrix pore structure in crystalline rocks and evidences for diffusion properties

Maikki Siitari-Kauppi
Laboratory of radiochemistry, Department of chemistry
Matrix diffusion studies begun late 80’s at HYRL:

- radionuclides transport properties in flow and in matrix
- radionuclides sorption on crushed rock material
- rock matrix characterisation on core scale; porosity, pore structure, PMMA method
- natural analogue studies
Content

Background
Definitions (porosity, pore structure, diffusivity)
Pore apertures /Anion exclusion
PMMA method
HTO and Cl-36 through diffusion
C-14 MMA out diffusion
Radionuclide transport in geosphere

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

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

\[ R_p = 1 + \frac{1 - \varepsilon_p}{\varepsilon_p} K_d \rho_s \]
Chemical diffusion in Geomaterials: why it is difficult to predict?

Pore network of rocks are complex PHYSICS
- Pore connectivity?
- Pore apertures?
- Pore tortuosity?
- Porosity vs. Diffusion?
- The scale problem

Solute - mineral interactions are complex CHEMISTRY
- Geochemical interactions
- Sorption
- Effect of pH, ionic force, dissolution/precipitation…
- Reactive transport: pore space change against time

GEOLOGY
In situ

**Scale**

- PMMA autoradiography
  - 100-2000 cm$^3$
- PET
- Water saturation porosimetry
  - 10-100 cm$^3$
- Mercury porosimetry, CT tomography
  - 1-10 cm$^3$

**Porosity increase**

Effective diffusion / pore diffusion connected / diffusion porosity

\[ \mathcal{E}_t = \mathcal{E}_f + \mathcal{E}_d + \mathcal{E}_r \]
Diffusion of solute in water  
(free diffusion)  

\[ J_F = -D_w \frac{\partial C}{\partial x} \]  

flux prop. to concentration gradient

Diffusion of solute in pore space
System of parallel tubes or plates:  
\[ J_P = -D_w \Phi \frac{\partial C}{\partial x} \]
effect of porosity

Real pore network:  
\[ J_{Po} = -D_w \Phi G \frac{\partial C}{\partial x} \]
porosity and geometry effects

C : concentration in porewater mol.l⁻¹
the proportionality factor is which is called \textit{Effective Diffusion} coefficient  
\[ D_w \Phi G = D_e \]
\[ D_p = \frac{\delta}{\tau^2} D_w = GD_w \]

**Figure 2.2** Schematic explanation of
a) tortuosity, which lengthens the diffusion pathway, and
b) constrictivity, which influences the diffusion cross-sections.
(Frick 1996)

\[ D_e = D_p \varepsilon_p = D_w G \varepsilon_p = D_w G_F \]
Porosity in geomaterials

• **PORES**
  - micropores < 2 nm
  - mesopores 2 nm – 50 nm
  - macropores > 50 nm

• **FISSURES**
  - long and narrow
  - intra- and intergranular
  - open or filled
  - up to micrometers

• **GRAIN BOUNDARIES and FRACTURES**
Anion exclusion
(after Mitchell, 1976 in Frick, 1993)

Simplified schematic representation of the bonding and distribution of water molecules and ions on silicate surfaces of the pore space and the relative viscosity of the aqueous phase in narrow pores.
Anion repulsion/exclusion
(after Mitchell, 1796 in Frick, 1993)

Schematic distribution of ions in the vicinity of the mineral surfaces. Approximate data on the extent (nm) of the diffusive double layer are obtained using Gouy-Chapman theory (Morel, 1983, p 404-407). Electrostatic interactions dominate in narrow pores. Anions are representative only to a limited extent of diffusion behaviour.
What was studied?
rock porosity, porosity versus mineralogy, morphology of pore space pores / fissures / fractures - tortuosity / constrictivity / pore apertures
connectivity – accessible pore space adjacent to the water flowing fracture
structure and mineralogical heterogeneities
diffusive properties

What were the methods?
• **PMMA autoradiographic method** + (particle tracking TDD)
• Petrographic analyses, optical microscopy, electron microscopy, confocal laser microscopy, energy dispersive X ray analyses
• CT microtomography
• Hg intrusion porosimetry, gas adsorption, water intrusion porosimetry
• He-gas method for permeability and diffusion
• through-diffusion/ in-diffusion with different probe molecules HTO, Cl, Na, Cs in water phase
Autoradiography

10 cm

PMMA autoradiographic method
PMMA porosity patterns in three granites - different shades of grey on the autoradiograph, represent different porosities, the darker the shade the higher the porosity.

- El Berrocal granite, Spain: 0.3%
- Grimsel granodiorite, Switzerland: 0.6%
- Palmottu granite, Finland: 0.7%
Pore apertures by Hg porosimetry

Incremental Intrusion vs Diameter

+ Incremental Intrusion
○ Cumulative Intrusion

Incremental Intrusion (mL/g)
Cumulative Intrusion (mL/g)

Pore apertures for Grimsel granodiorite

Incremental Intrusion vs Diameter

+ Incremental Intrusion
○ Cumulative Intrusion

Incremental Intrusion (mL/g)
Cumulative Intrusion (mL/g)

pore apertures for in situ PMMA impregnated Grimsel granodiorite
Pore apertures from autoradiographs with image analyses and by SEM

Microcrack aperture histogram of “Kuru TK LAB 1”

- Ouverture maximale
- Ouverture minimale
- MEB

Microcrack aperture histogram of “Grimsel TK LAB”

- Ouverture maximale
- Ouverture minimale
- MEB

Normalized frequency

Size bin (µm)
Muscovite granite, boulder from Hämeenlinna
0.8%
PMMA porosity patterns
In three granites
-different shades of grey on the autoradiograph, represent different porosities, the darker the shade the higher the porosity

R38 Olkiluoto
diatextic gneiss
0.2%

R38 Olkiluoto
pegmatite granite
0.4%

4 cm
Veigned gneiss
(Repro 323) 0.4%

4 cm
Veigned gneiss
(Repro 323)
0.6%
KR4 623 m 0.2%
Through diffusion experiments

Figure 6. During the through-diffusion experiment diffusion takes place between a tracer-containing solution and a tracer-free solution through the sample studied.
Out-Leaching Technique for Characterizing Pore Fluids in Crystalline Rocks

Distilled water (about 55 ml) having no initial chloride is placed into the reservoir (1 mm wide water zone) and the water is changed every 14 days. Concentration will increase as chloride from rock pore space moves into the reservoir by diffusion.

In situ water saturated rock core having an initial chloride pore-water concentration of about 5 g/l
- about 30 cm in height
- 4.2 cm in diameter
- porosity of 0.4 % >> total amount of chloride in the matrix pore water about 10 mg
Olkiluoto tonalite 68.0m
(through diffusion 277 d)

\[ D_e(\text{HTO}) = 1.3 \times 10^{-13} \text{m}^2/\text{s}, \alpha(\text{HTO}) = 0.3 \% \]
\[ D_e(\text{Cl-36}) = 1.3 \times 10^{-14} \text{m}^2/\text{s}, \alpha(\text{Cl-36}) = 0.05 \% \]
\[ D_a(\text{HTO}) = 0.5 \times 1.5 \times 10^{-10} \text{m}^2/\text{s} \]
\[ D_a(\text{Cl-36}) = 2.4 \times 10^{-11} \text{m}^2/\text{s} \]

Into tonalite matrix
25% of HTO
21% of Cl-36

Out of tonalite matrix
4.5% of HTO
0.5% of Cl-36
Comparison of the through-diffusion of HTO and chloride in two samples; mica gneiss and basalt having porosities of 0.2 and 2%

**Figure 2.** Through-diffusion results: measured normalized diffused tracer $A/A_0$ (%) versus diffusion time for HTO (squares) and $\text{Cl}^-$ (circles) through 0.5 cm of basalt; derived eff. diffusivities: $1\cdot10^{-14}$ m$^2$/s (HTO) and $0.1\cdot10^{-14}$ m$^2$/s ($\text{Cl}^-$), respectively; measured porosity: 2%.

**Figure 3.** Through-diffusion results: measured normalized diffused tracer $A/A_0$ (%) versus diffusion time for HTO (squares) and $\text{Cl}^-$ (circles) through 1.3 cm of mica gneiss (Sievi, Sy1 282 m); derived eff. diffusivities: $1\cdot10^{-14}$ m$^2$/s (HTO) and $0.1\cdot10^{-14}$ m$^2$/s ($\text{Cl}^-$), respectively; measured porosity: 0.2%.

Outleaching of $^{14}$C-MMA (Kivetty, unaltered porphyritic granodiorite) - out diffusion occurs mainly along transgranular fissures which form the main connective network of porosity.

Ki7_21
$D_a = 6.8 \times 10^{-11} \text{ m}^2/\text{s}$

![Graph showing diffusion data](image)
Outleaching of $^{14}$C- MMA (Kivetty, slightly altered porphyritic granodiorite) - diffusion occurs mainly along transgranular fissures but porosity is increased due to alteration / intragranular porosity exists.

$D_a = 11 \times 10^{-11} \text{ m}^2/\text{s}$

Ki7_25

Experimental
Theoretical maximum
Fit by short time $\rightarrow D_a$
Fit to longer times with same $D_a$
Outleaching of $^{14}$C-MMA (Kivetty, altered porphyritic granodiorite) - due to strong alteration the complexity of pore structure increases, intragranular porosity has significant role in connected pore network.

$\text{Ki7}_122$

$D_a = 1.8 \times 10^{-11} \text{ m}^2/\text{s}$

$D_a = 0.7 \times 10^{-11} \text{ m}^2/\text{s}$

$A(t)/A_0$ vs $\sqrt{t}$

- Experimental
- Fit by short time $\rightarrow D_a$
- Low $D_a$ from long time
- High $D_a$ from short time
- Theoretical maximum
He gas diffusion measurements (through diffusion) for Finnish granites (data from 90’s)
Conclusions

- Interconnected porosity was detected for the studied rocks in core scale at lab by PMMA method, exceptions were some gneissess from Olkiluoto.
- In situ porosity was found to be about 30-40% lower than porosities measured at lab for Grimsel Granodiorite.
- Anion exclusion was pronounced for mica gneiss and tonalite >> micro (<2 nm) and meso (<50 nm) pores.
- Anion exclusion was minor for fresh pegmatite granite >> micro fissures (~≥ 1 µm).
- He porosity was lower than tritium porosity for tonalite and mica gneiss >> micro and meso pores.
Thank you!