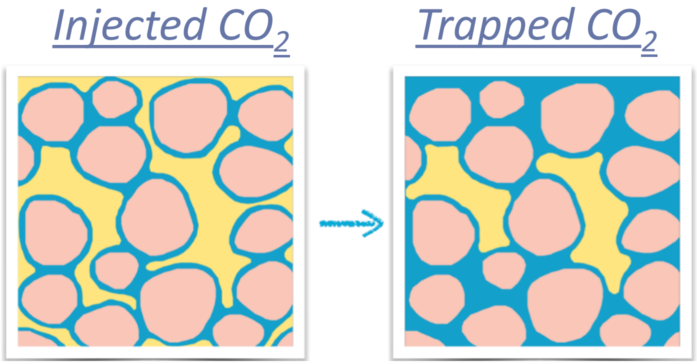
The Long-term Redistribution of Residually Trapped CO_2 by Ostwald Ripening

Yaxin Li, Charlotte Garing, Sally M Benson

Nov 7th 2019

Long-term fate of residually trapped CO_2 is unclear

- Residual trapping traps CO_2 in the form of disconnected ganglia by capillary forces.



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  - assumed to be permanent in simulation
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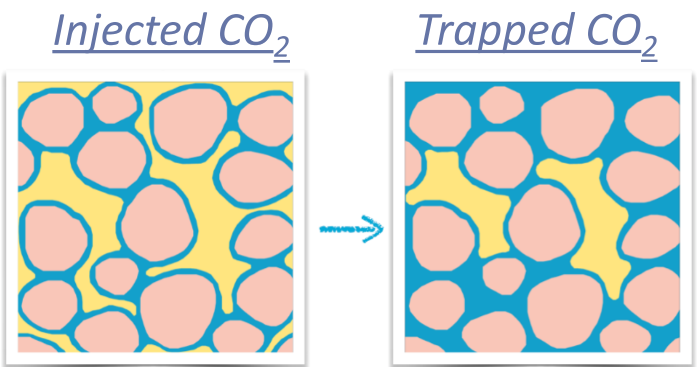

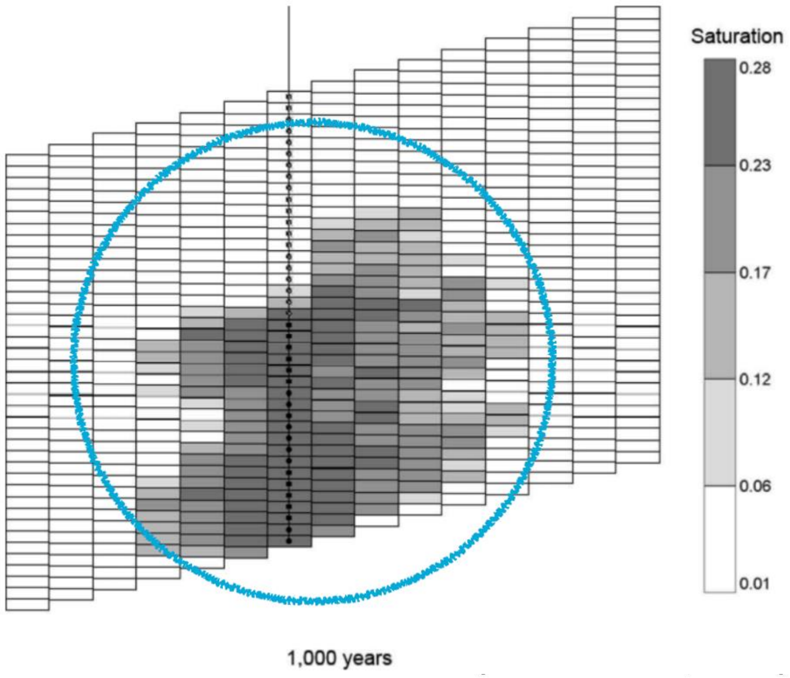

Kumar et al., 2005

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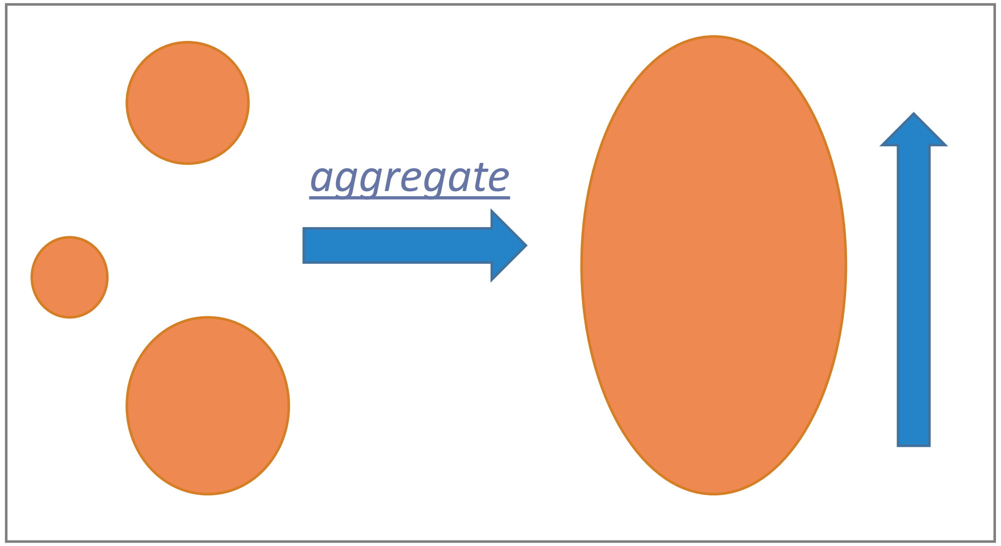

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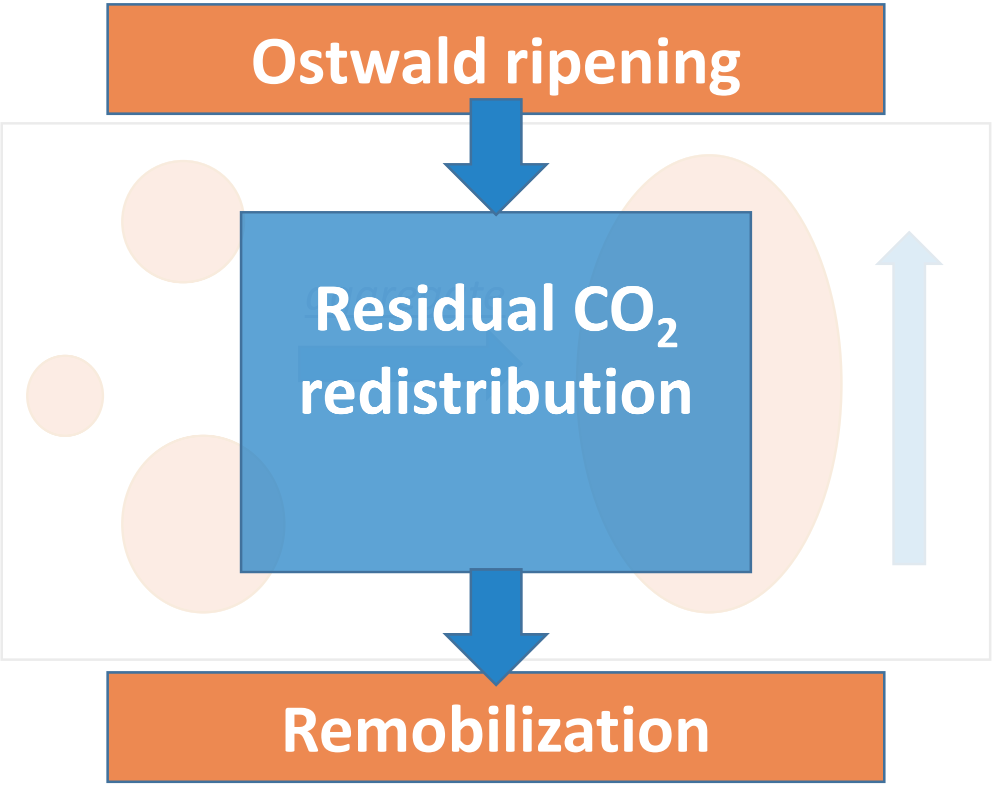
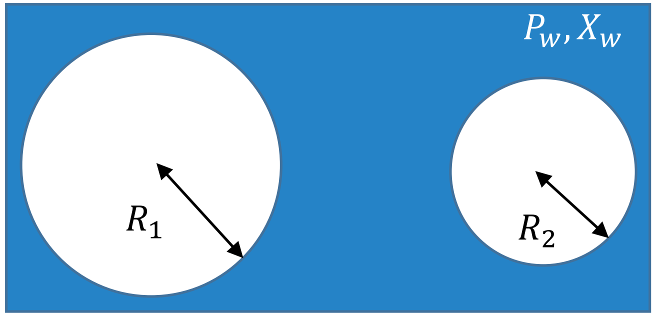


Ostwald ripening may serve as a mechanism to redistribute residual CO_2

In a bulk liquid

Initial condition



Mechanism of Ostwald ripening

Interfacial curvature difference

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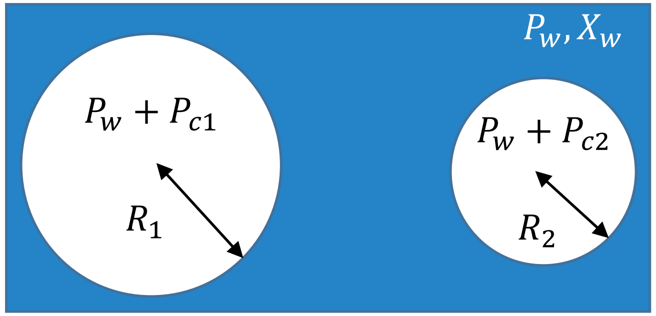

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$$P_c = \frac{2\sigma}{R}$$

Capillary pressure difference

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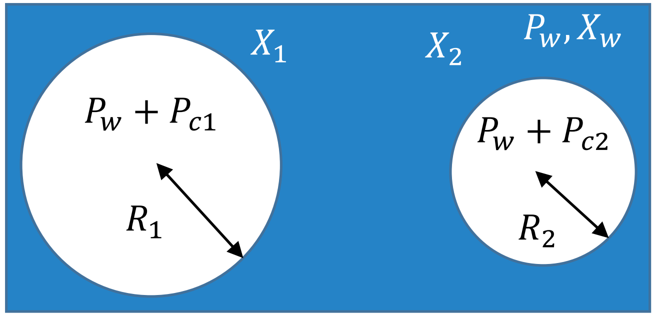

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$$X = H(P_w + P_c)$$

CO_2 mass fraction gradient in the aqueous phase

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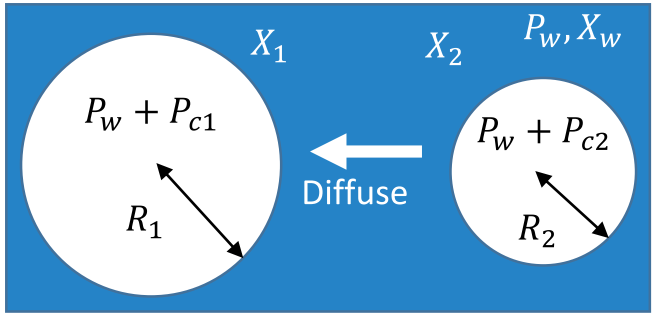

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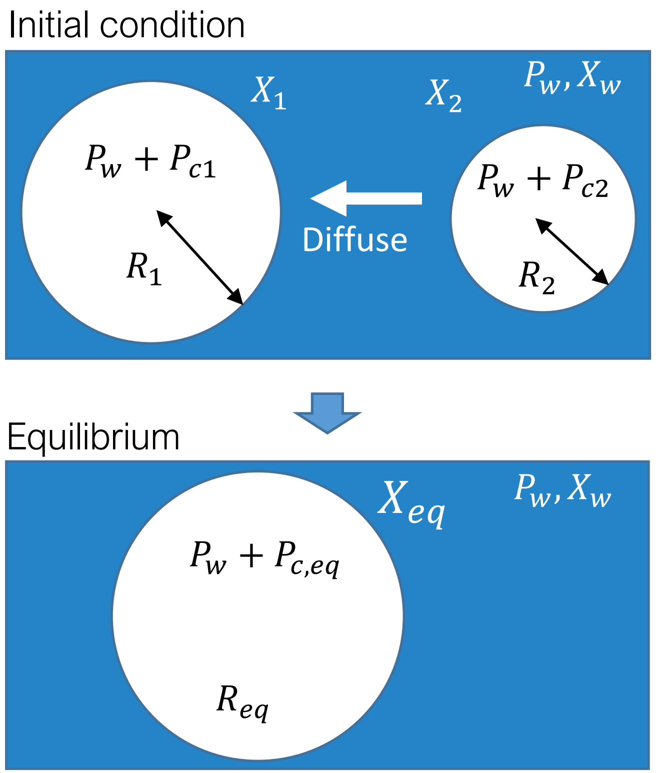

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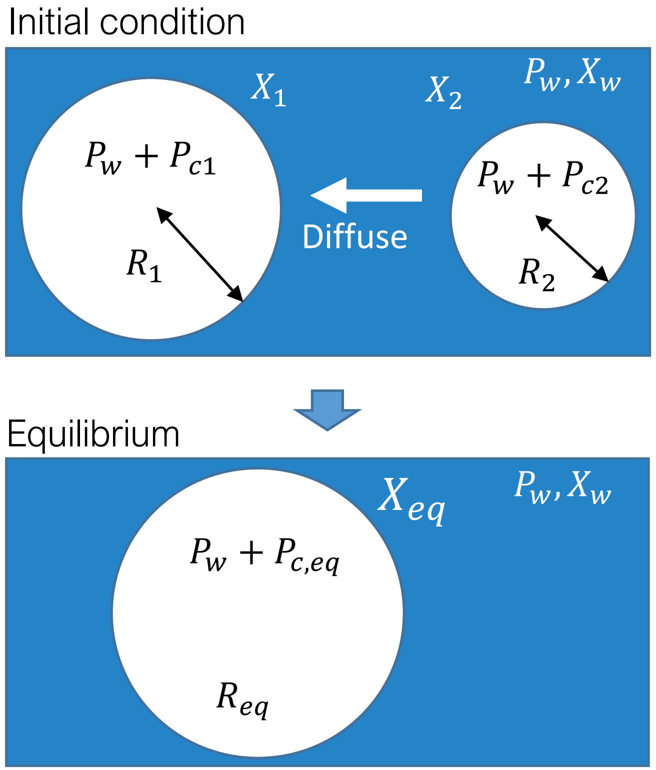

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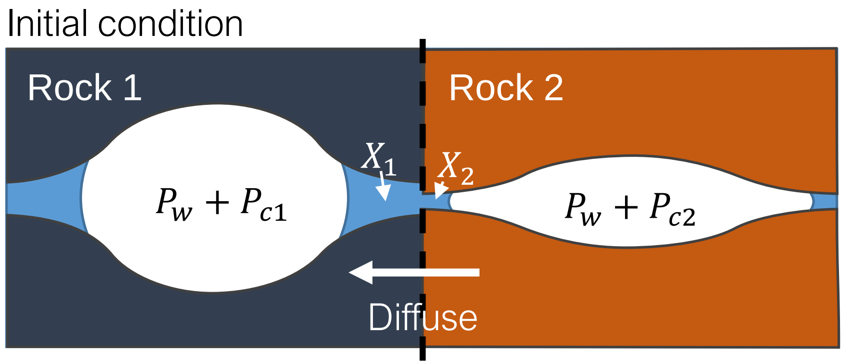

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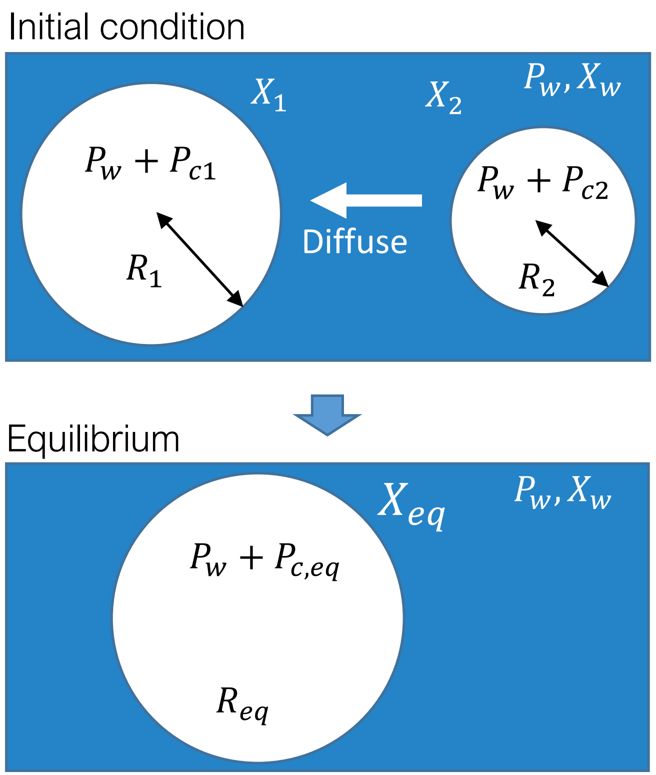

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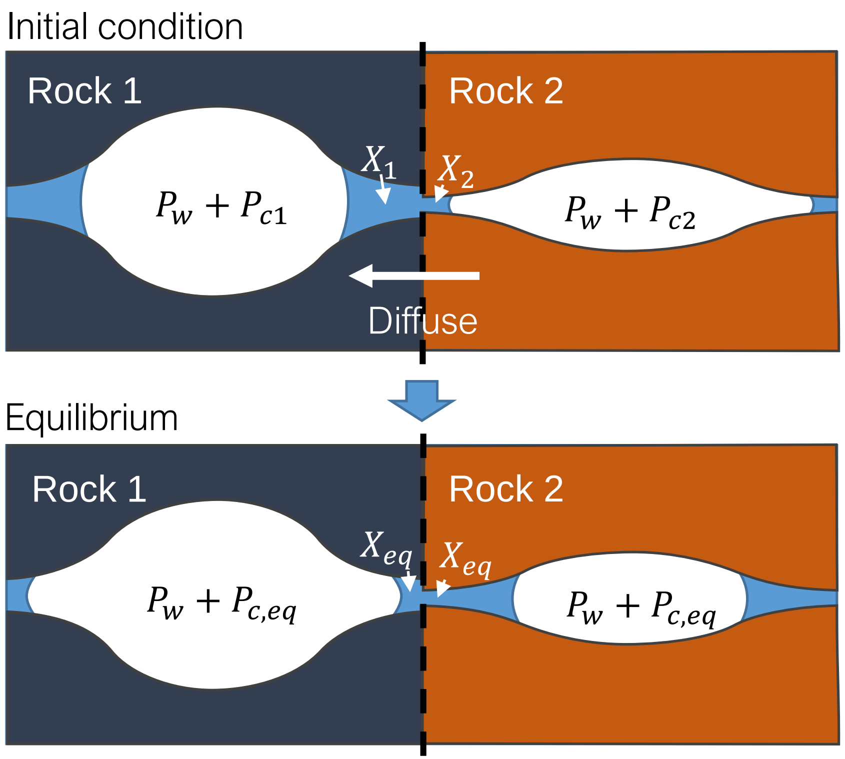
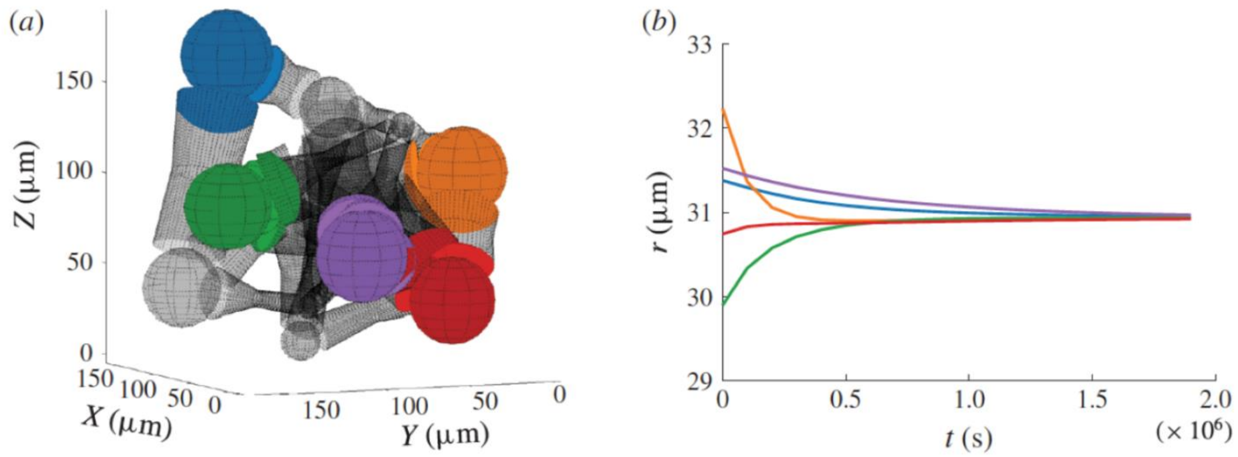


Take a closer look at trapped CO_2 ganglia…

- Adjacent ganglia can approach an **equilibrium capillary pressure**



de Chalendar et al., 2017

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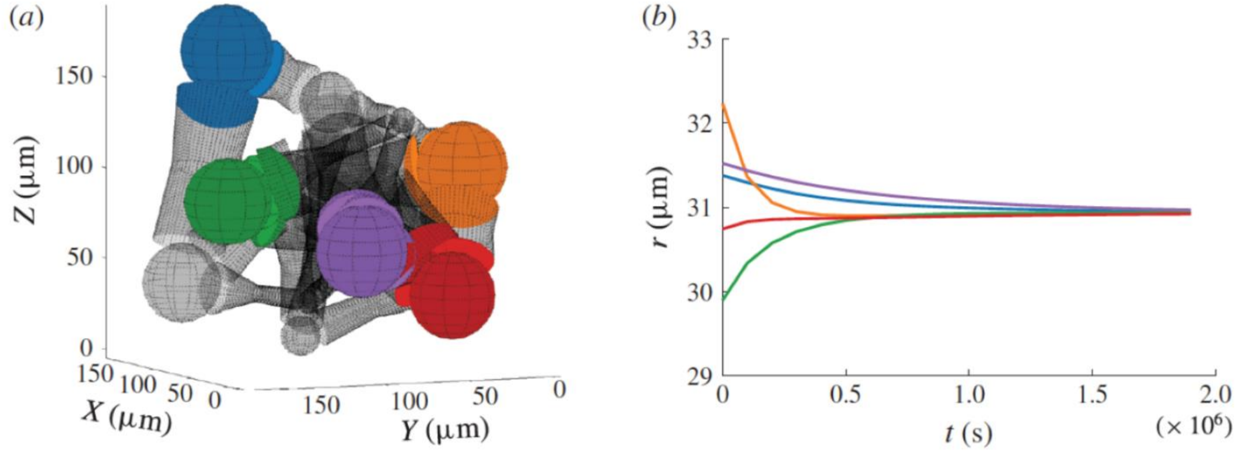

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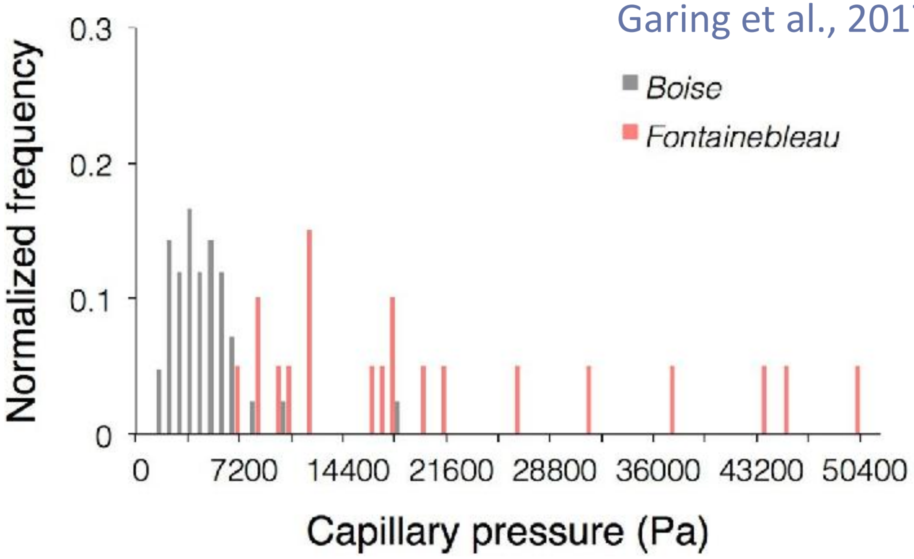
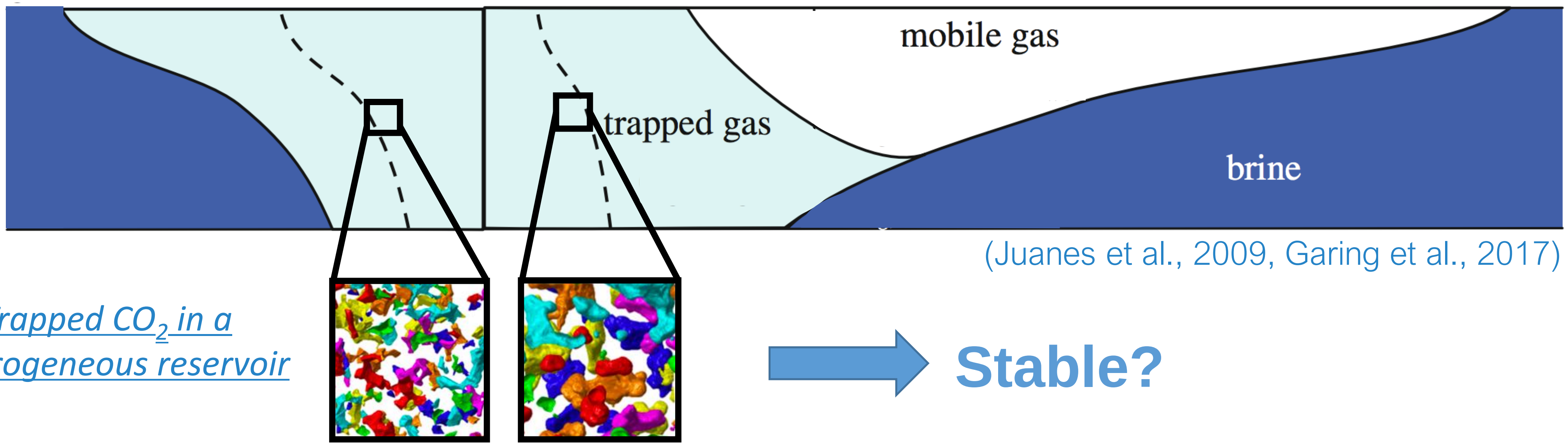
- This local **equilibrium capillary pressure varies** in different porous media, roughly at the order of the entry pressure.

Garing et al., 2017



Capillary pressure gradients may initiate Ostwald ripening among residual CO_2 in a heterogeneous reservoir

Conceptual representation of CO_2 migration



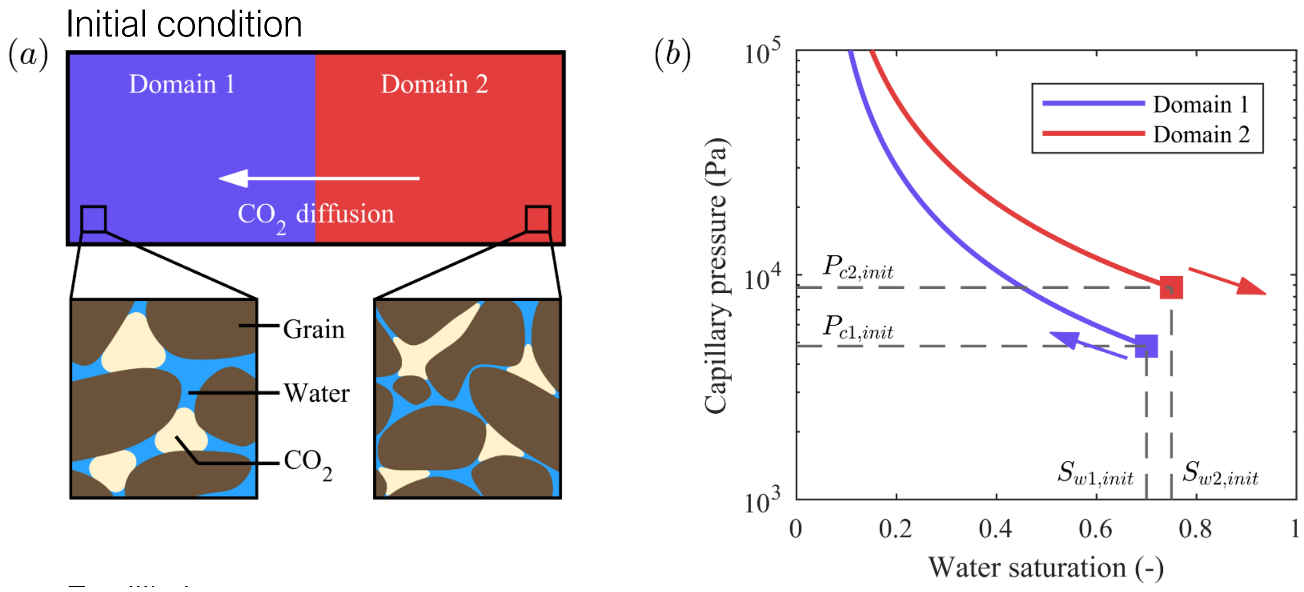
(Juanes et al., 2009, Garing et al., 2017)

Trapped CO_2 in a heterogeneous reservoir

Stable?

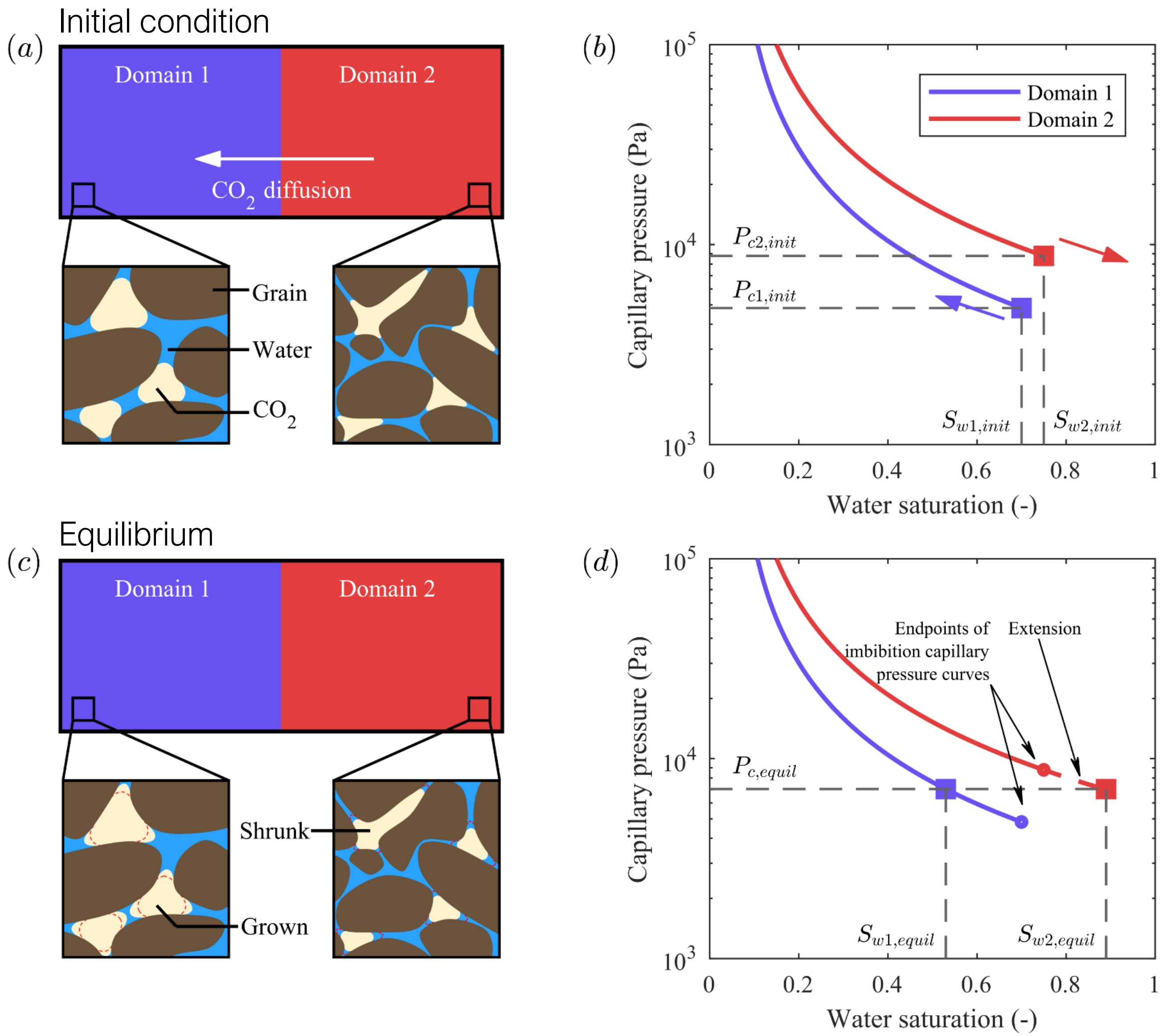
The conceptual model of Ostwald ripening at the continuum scale

- Two adjacent domains with different capillary pressure curves
- Initial condition – the end of imbibition



The conceptual model of Ostwald ripening at the continuum scale

- Two adjacent domains with different capillary pressure curves
- Initial condition – the end of imbibition
- CO_2 diffuses in the aqueous phase driven by the capillary pressure gradient
- At equilibrium, the capillary pressure gradient has disappeared, and the residual CO_2 saturation has changed



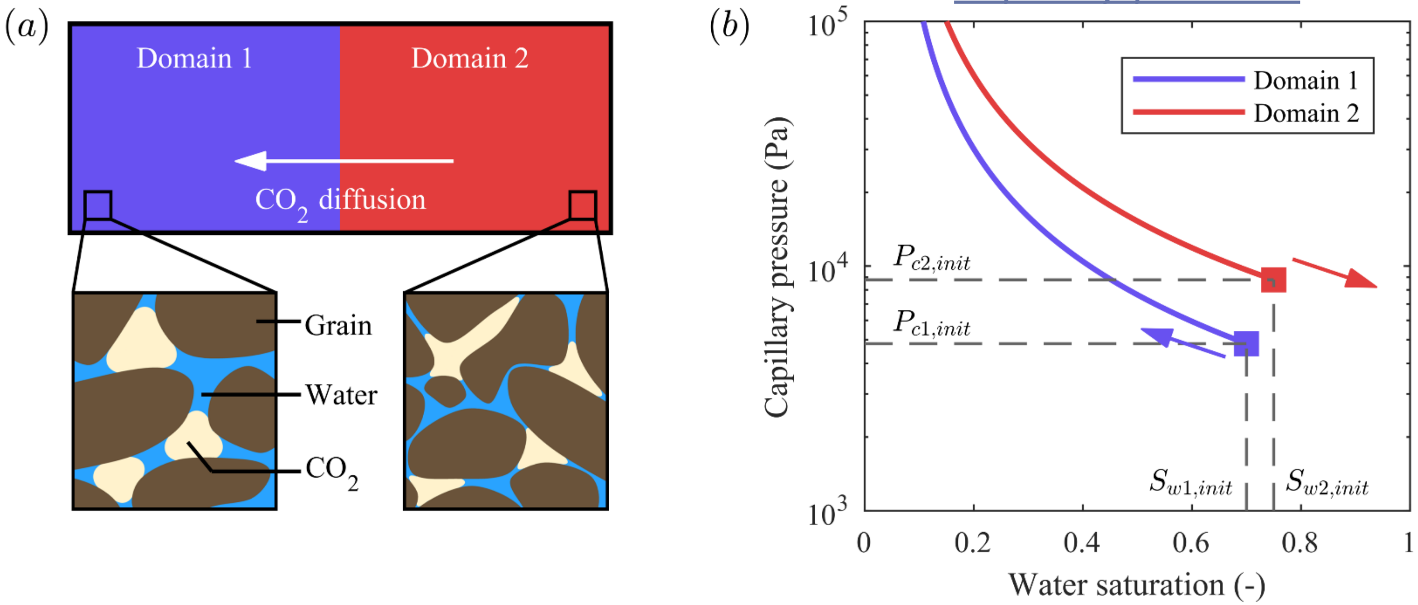
Research questions

- **Can capillary pressure gradient drive Ostwald ripening among residual CO_2?**

Numerical simulation on Ostwald ripening

- TOUGH2 – ECO2N
- Use the same conceptual model
  - 1d horizontal model with closed boundary
  - Two domains follow different capillary pressure
  - The initial condition is at the end of imbibition

[Capillary pressure]



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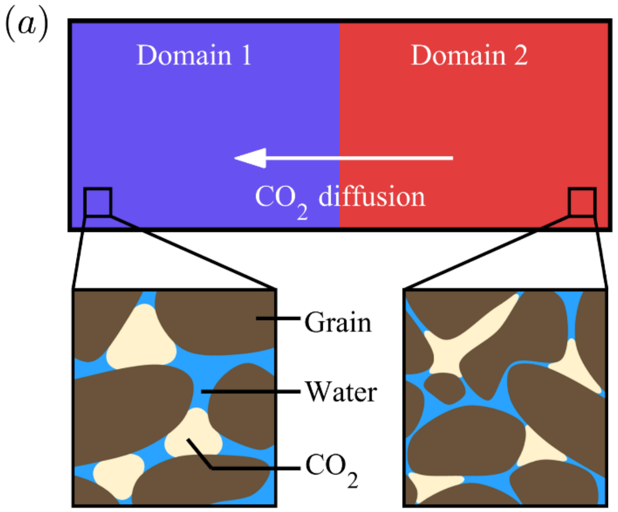
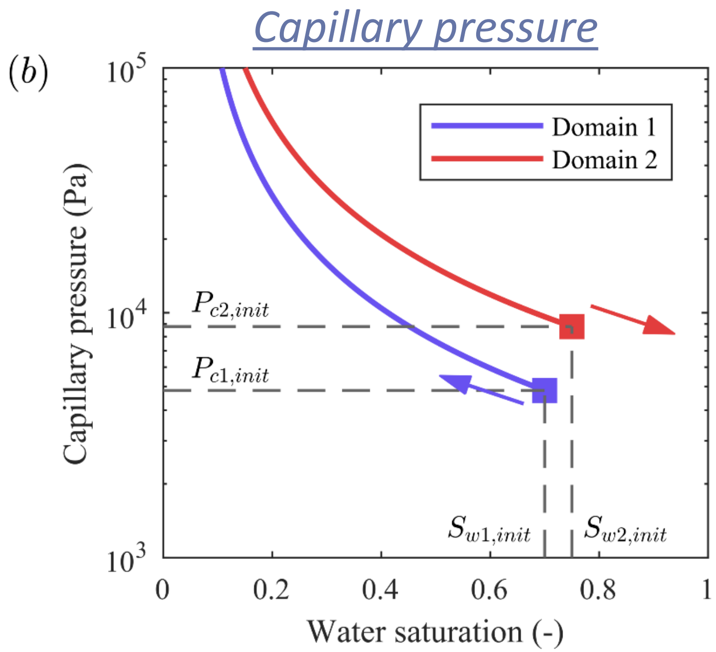
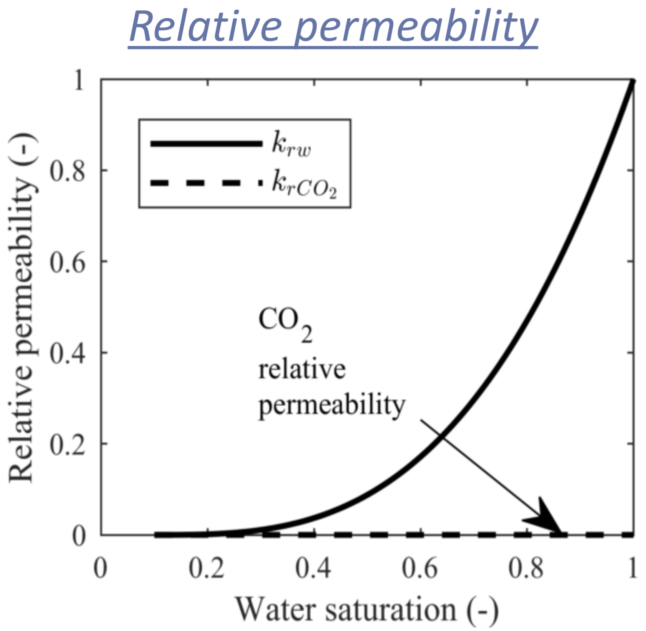
- CO_2 relative permeability is set to zero

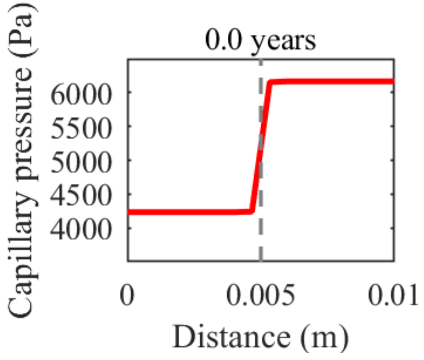






Residual CO_2 is redistributed by Ostwald ripening even if it is completely immobile, but the progress is extremely slow

(a) Initial condition



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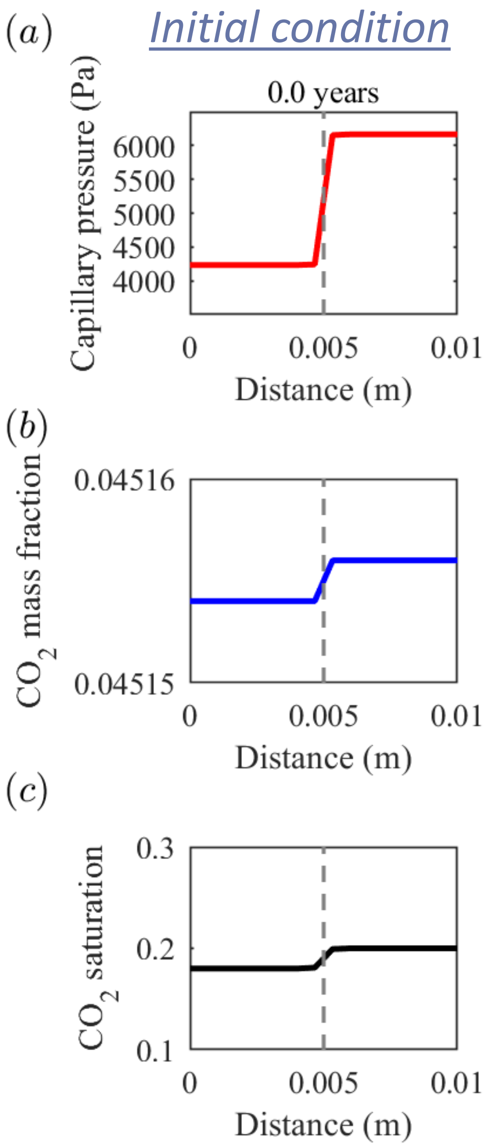

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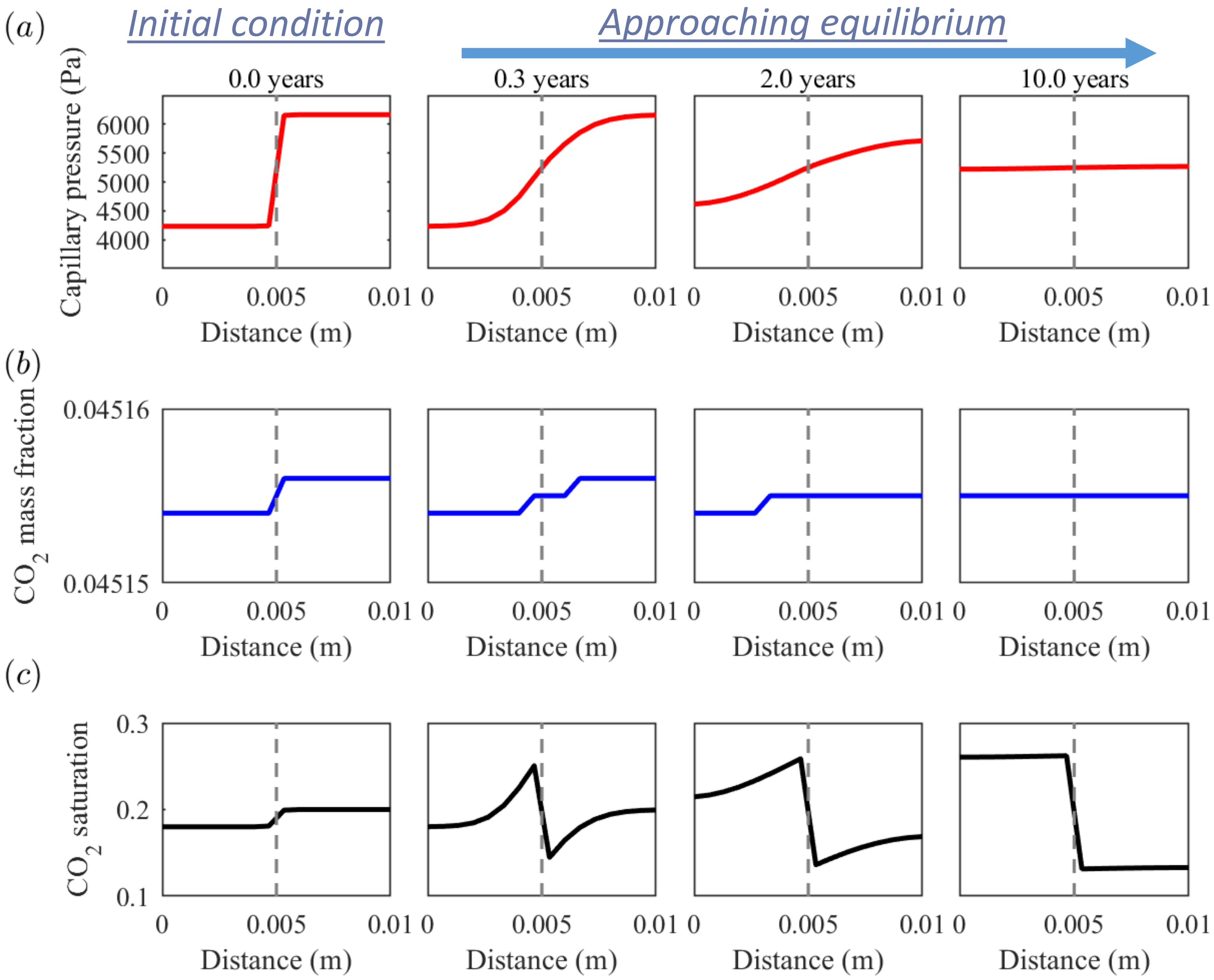

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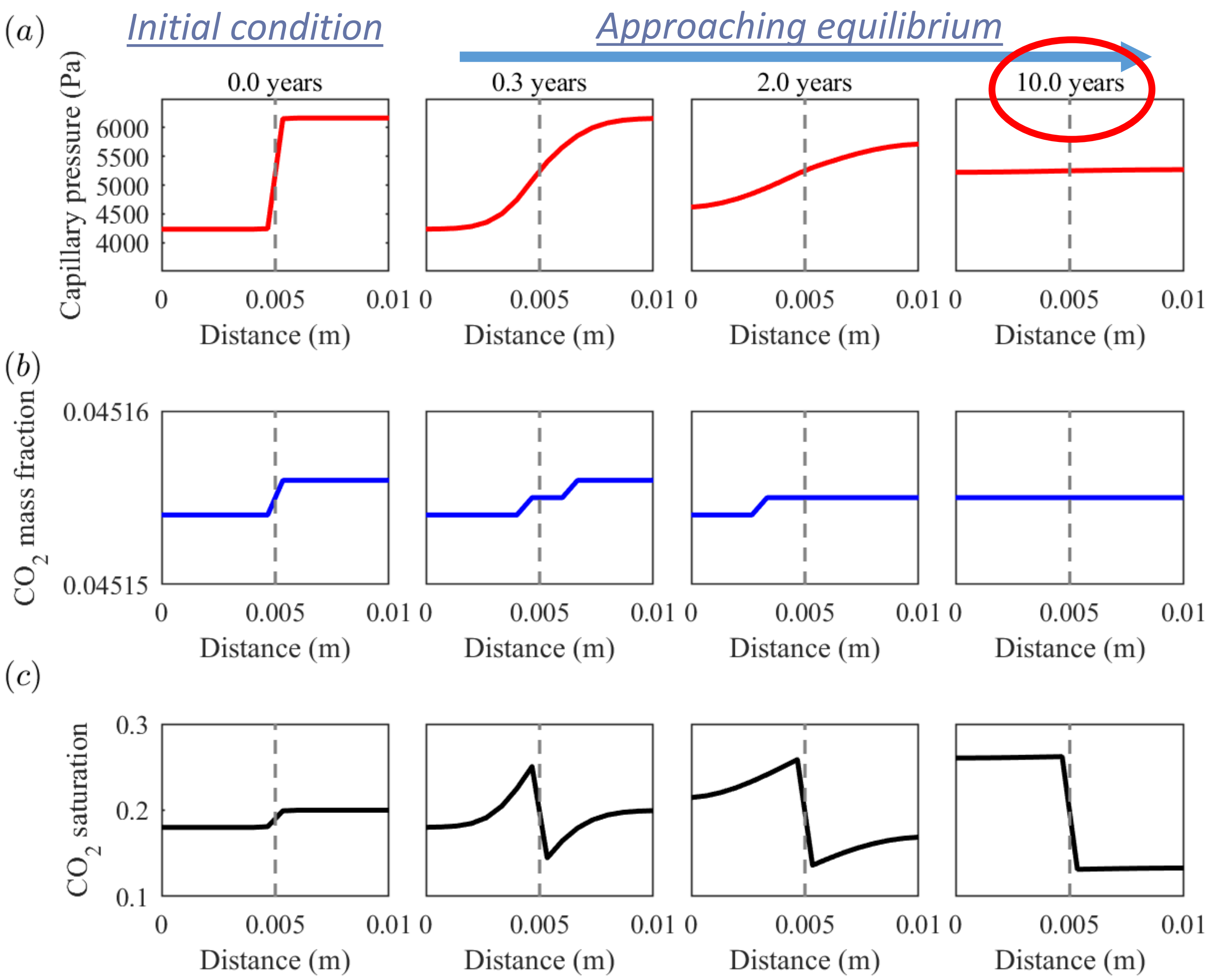

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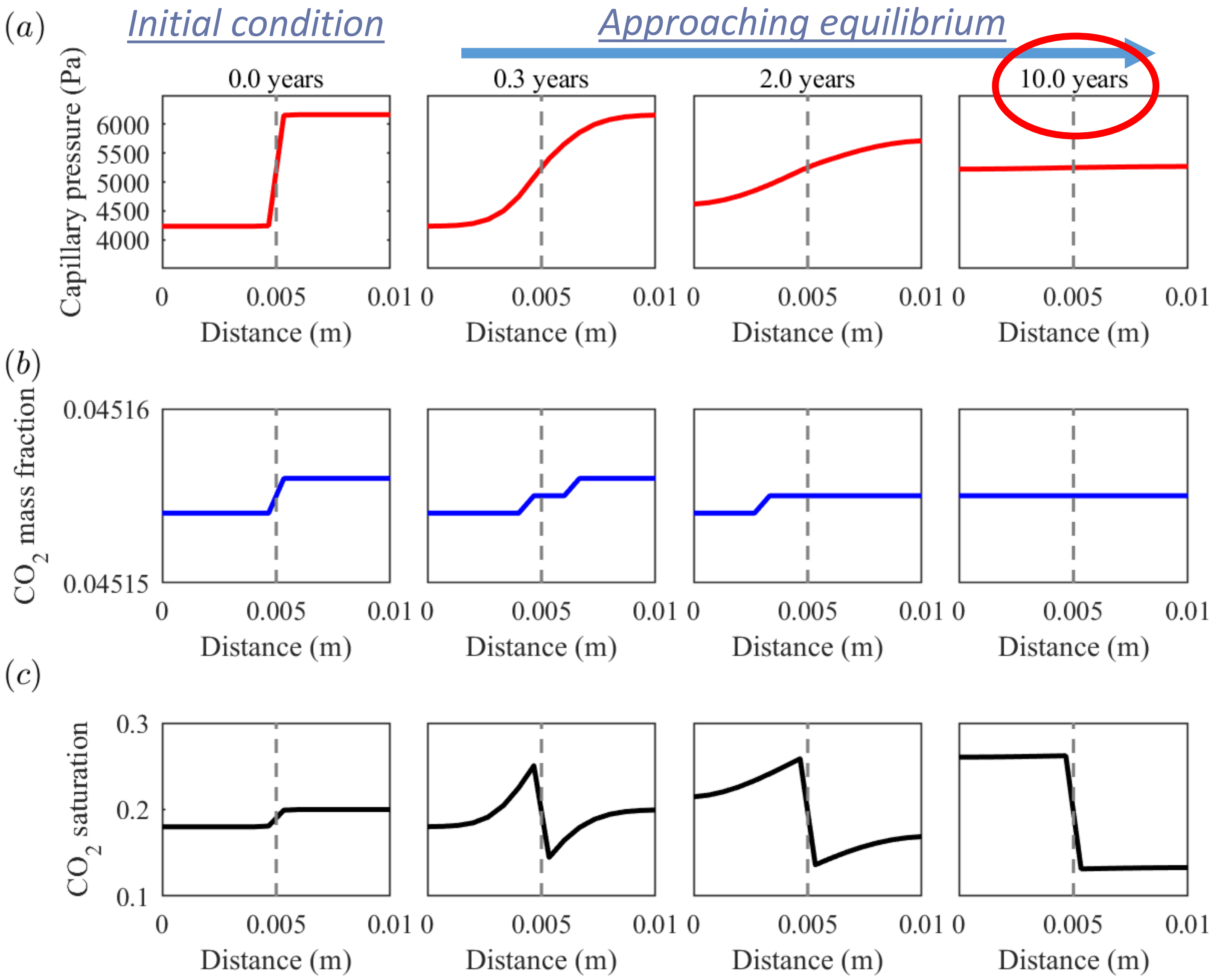

Compare to a single-phase diffusion problem

- Single-phase diffusion problems
  - No separate-phase CO_2
  - Only the aqueous phase with dissolved CO_2

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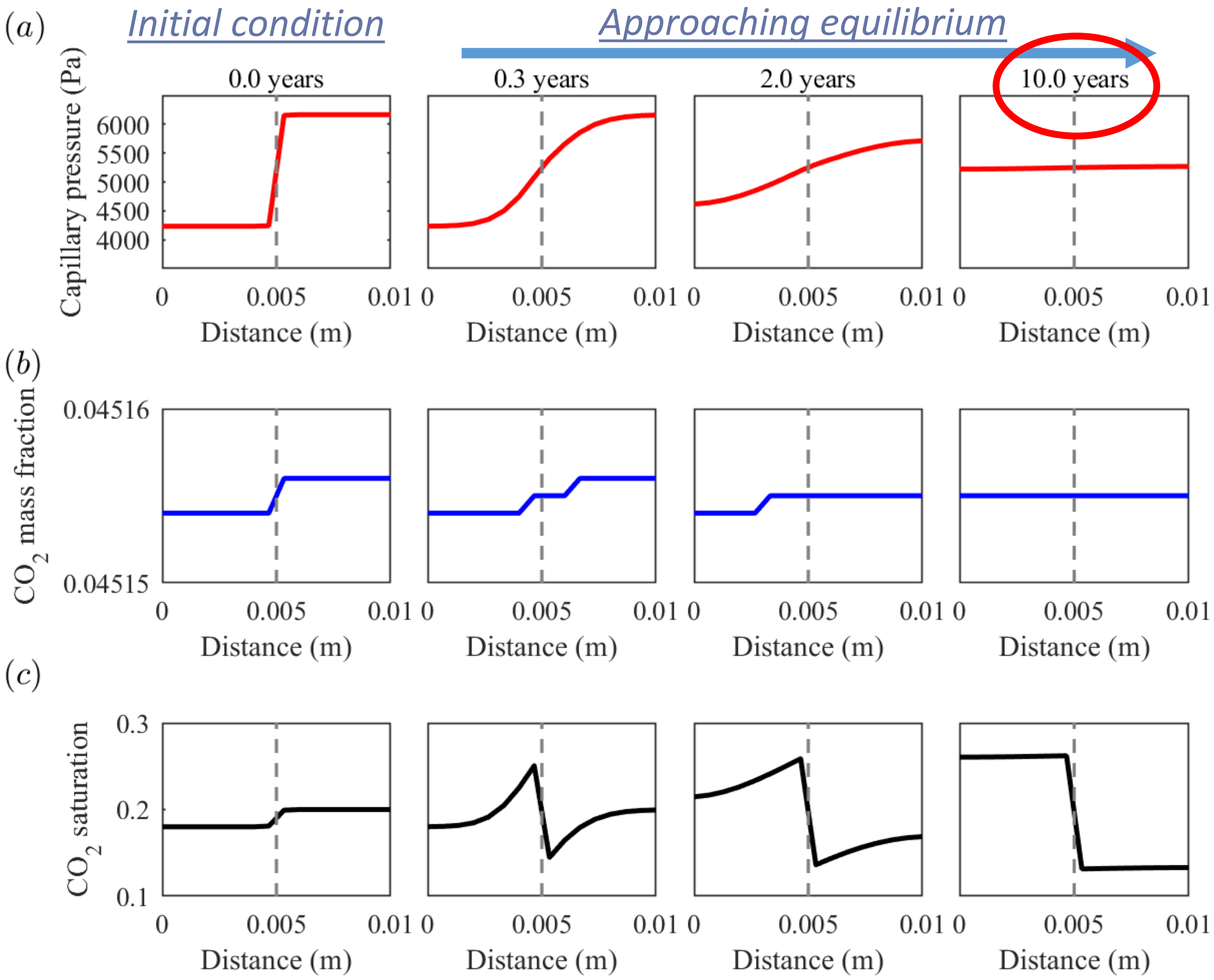

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- Characteristic time
  - $t_c = \frac{l^2}{D} = \frac{(0.005\ m)^2}{5\times10^{-9}} \sim 1\ hr$
  - But we have 10 years here…

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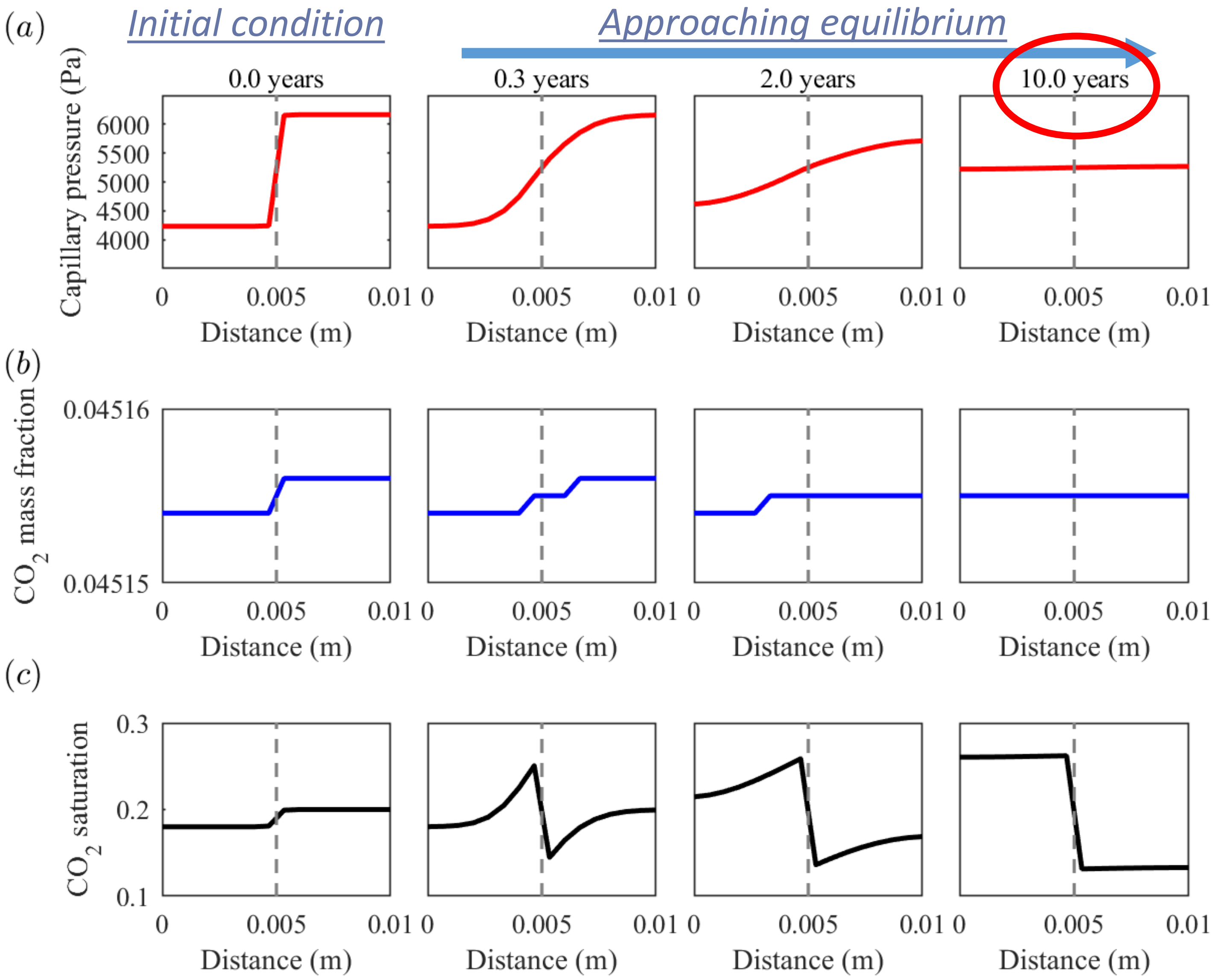

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The time to approach equilibrium is 10^5 times longer than a single-phase diffusion problem!

Research questions

- **Can capillary pressure gradient drive Ostwald ripening among residual CO_2?**
  - Yes. Capillary pressure gradient can drive Ostwald ripening among residual CO_2 groups. However, the time for equilibration is significantly longer than that for single-phase diffusion problems.

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- **Why is there a discrepancy of time scale between Ostwald ripening and single-phase diffusion problems?**

Diffusion equation of Ostwald ripening – find X(x, t)

- Mass conservation equation

$$\frac{\partial(XS_w\rho_w\phi)}{\partial t}+\frac{\partial(YS_g\rho_g\phi)}{\partial t}=\frac{\partial}{\partial x}[\phi D_w S_w\frac{\partial(X\rho_w)}{\partial x}]$$

- Assumptions
  - Constant density, pure CO_2 in the gaseous phase and $S_w \sim 1$

$$\frac{\partial X}{\partial t}+\frac{\rho_g}{\rho_w}\frac{\partial S_g}{\partial t}=D_w\frac{\partial^2 X}{\partial x^2}$$

where

$$\frac{\partial S_g}{\partial t}=\frac{dS_g}{dP_c}\frac{dP_c}{dX}\frac{\partial X}{\partial t}$$

- Final form of the diffusion equation

Retardation factor

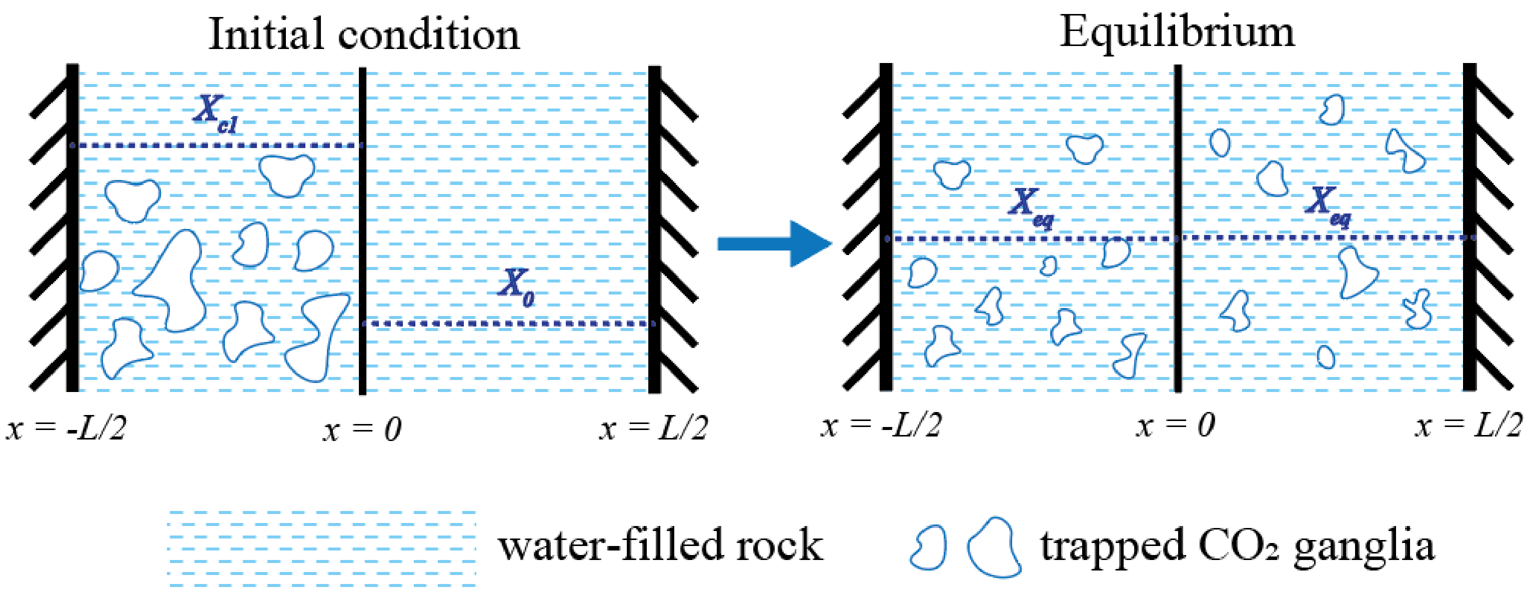
$$R_{CO_2}\frac{\partial X}{\partial t}=D_w\frac{\partial^2 X}{\partial x^2}$$

where

$$R_{CO_2}=1+\frac{\rho_g}{\rho_w}\frac{dS_g}{dP_c}\frac{dP_c}{dX}$$

An analytical solution X(x, t) to the diffusion equation for a homogeneous system

- Solve for a homogeneous case
  - reserves the characteristic of heterogeneous system
  - avoids non-linearity and discontinuity



Retardation factor in the homogeneous system

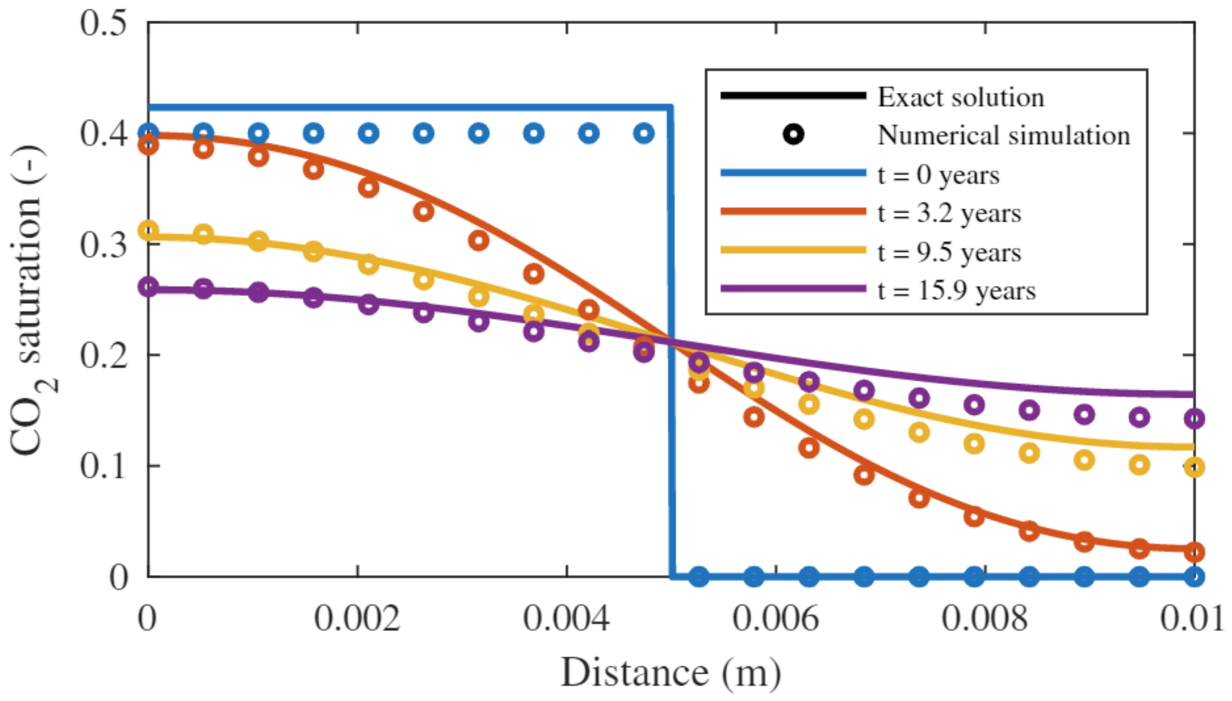
$$\boxed{R_{CO_2} = 1 + \frac{\rho_g}{\rho_w}\frac{P_w}{X_0}\frac{H_{tangent}}{H_0}\frac{1}{b}}$$

An analytical solution X(x, t) to the diffusion equation for a homogeneous system

- The analytical solution captures the transient CO_2 mass fraction profile of the system

$$X(x,t) - X_0 = \frac{1}{2}(X_{c1} - X_0) \sum_{n=-\infty}^{\infty} \{erf \frac{L/2 + 2nL - x}{2\sqrt{D_{equiv} t}} + erf \frac{L/2 - 2nL + x}{2\sqrt{D_{equiv} t}}\}$$

(Crank 1975)



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The equilibration is significantly retarded by the existence of separate-phase CO2

- Check the characteristic time

$$t_{c,single-phase} = \frac{l^2}{D_w}$$

$$t_{c,two-phase} = \frac{l^2}{D_{equiv}} \quad \text{where} \quad D_{equiv} = \frac{D_w}{R_{CO_2}}$$

$$t_{c,two-phase} = R_{CO_2} t_{c,single-phase}$$

- Check the order of magnitude of the retardation factor

Retardation factor in the homogeneous system

$$\boxed{R_{CO_2} = 1 + \frac{\rho_g}{\rho_w}\frac{P_w}{X_0}\frac{H_{tangent}}{H_0}\frac{1}{b}}$$

$$R_{CO_2} \sim (1 + 10^{-1} \times 10^9 \times 1 \times 10^{-3}) \sim \boxed{10^5}$$

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- **Why is there a discrepancy of time scale between Ostwald ripening and single-phase diffusion problems?**
  - The separate-phase CO_2 serves as an adsorptive material to retard the progress of diffusion, roughly by the order of 10^5. Its magnitude may vary depending on reservoir conditions and initial conditions.

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- **How to find the time scale of residual CO_2 redistribution in heterogeneous systems?**

An approximate solution is derived to predict the time scale of Ostwald ripening in heterogeneous systems

- Focus more on the amount of CO_2 transported instead of saturation profiles
  - Assume that CO_2 mass fraction is a step function within the two domains
  - Take into consideration that the diffusive flux is strong at the early stage

$$t = \frac{[\frac{1}{\phi_1(1-S^{init}_{CO_2,1})} + \frac{1}{\phi_2(1-S^{init}_{CO_2,2})}]\rho_g \phi_1 L^2 \alpha P_w H_{tangent}}{4\rho_w D_w X_0 H_0}$$

$$\times \int_{S^{init}_{CO_2,1}}^{S^*_{CO_2,1}} \frac{1}{P_{c2}(S_{CO_2,2}(S_{CO_2,1})) - P_{c1}(S_{CO_2,1})})d(S_{CO_2,1}).$$

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constant $\rightarrow$

- reservoir properties
- reservoir conditions
- initial conditions

integration $\rightarrow$

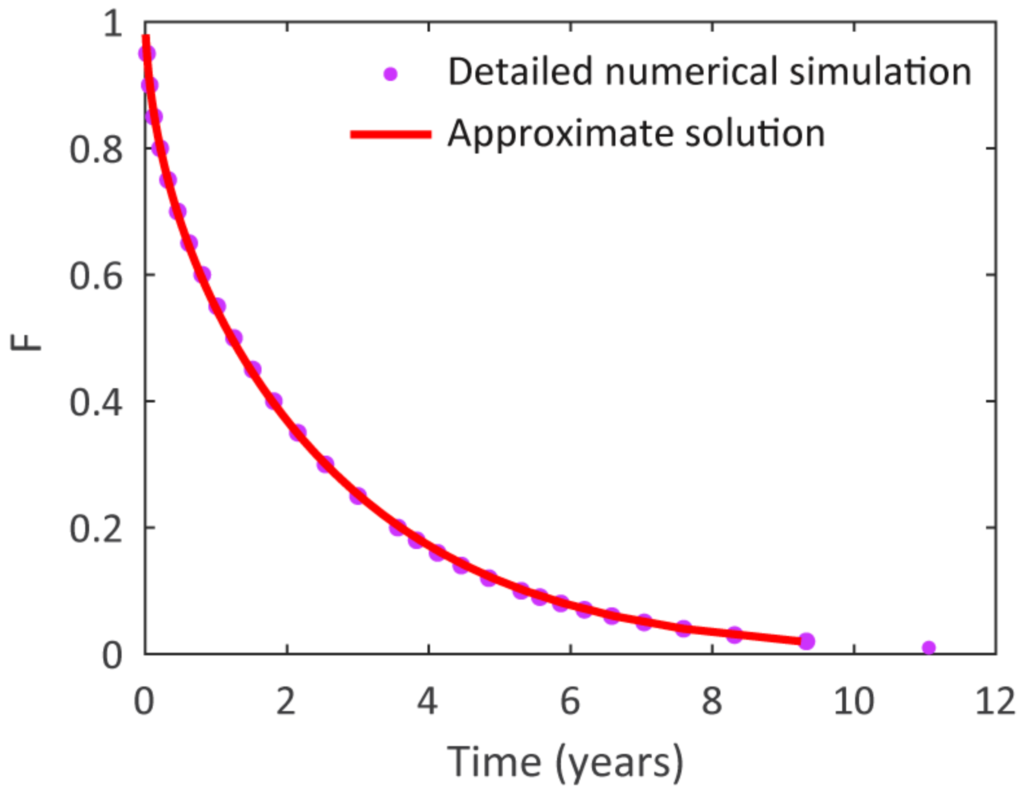
- Track the progress of Ostwald ripening during equilibration

The approximate solution can keep track of the progress of Ostwald ripening and predict the time at any stages

- Define an indication of progress on equilibration
  - The remaining fraction of capillary pressure gradient

$$\boxed{F = \frac{P_{c2}(t) - P_{c1}(t)}{P_{c2}^{init} - P_{c1}^{init}}}$$

The approximate solution achieves close agreement with numerical simulation



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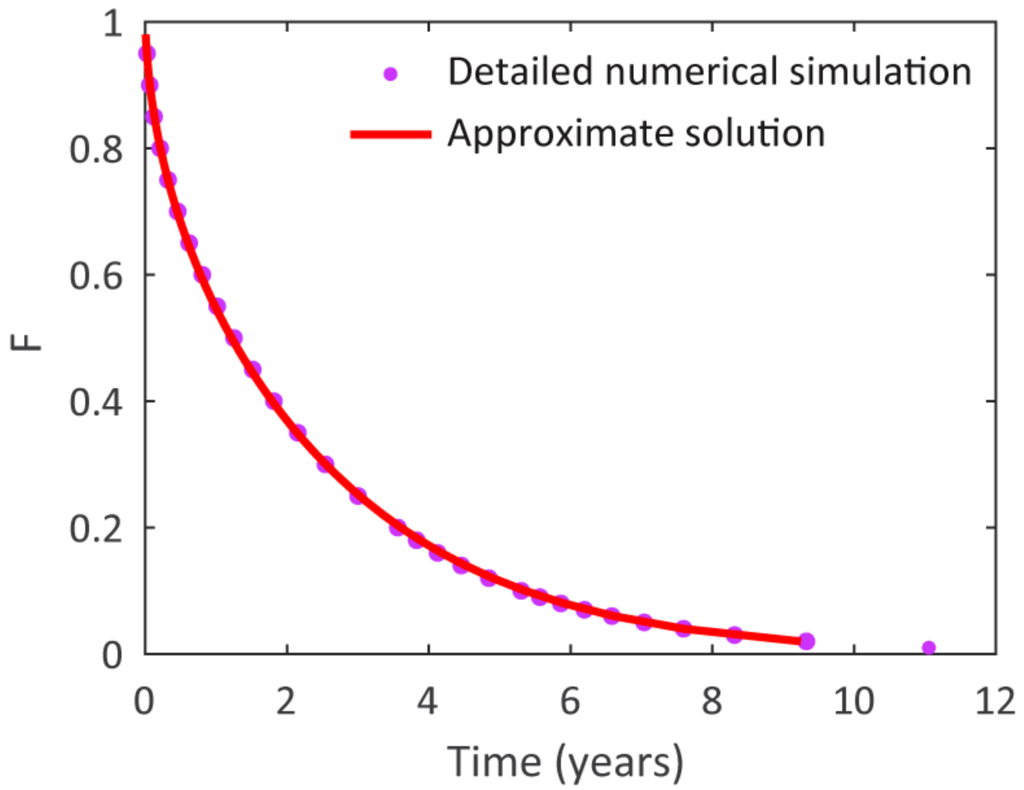
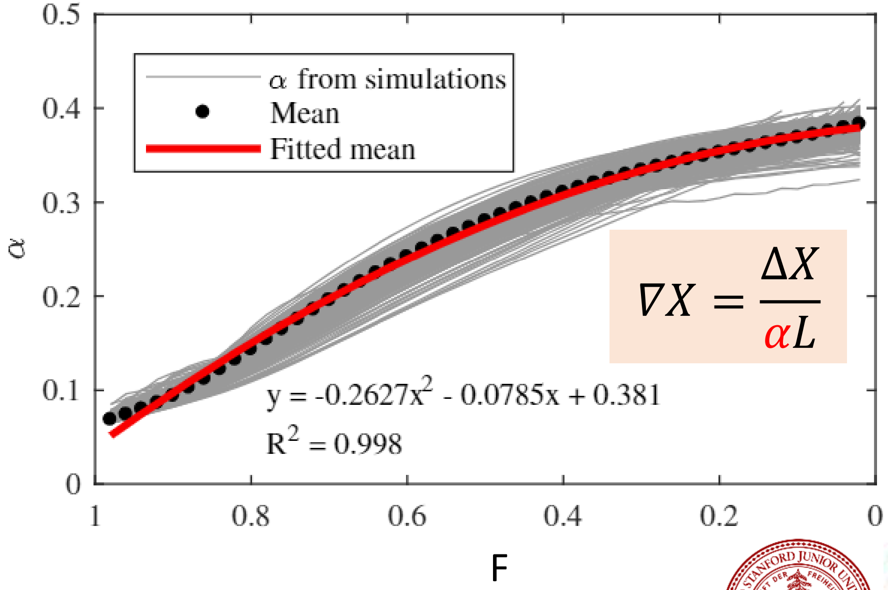


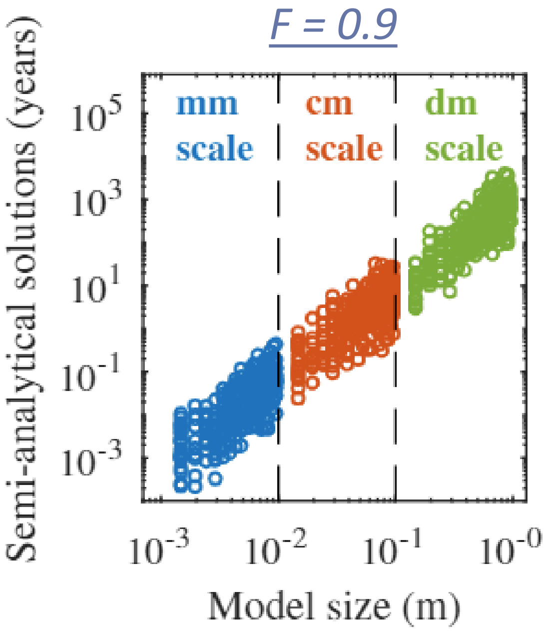
Correction on the diffusion length



Implications for geological CO_2 storage

- Ostwald ripening among residual CO_2 can occur driven by capillary pressure gradient
- It is a very slow process
  - Days to years for millimeter scales
  - Over thousands of years for meter and larger scales

Time scale for different spatial scales



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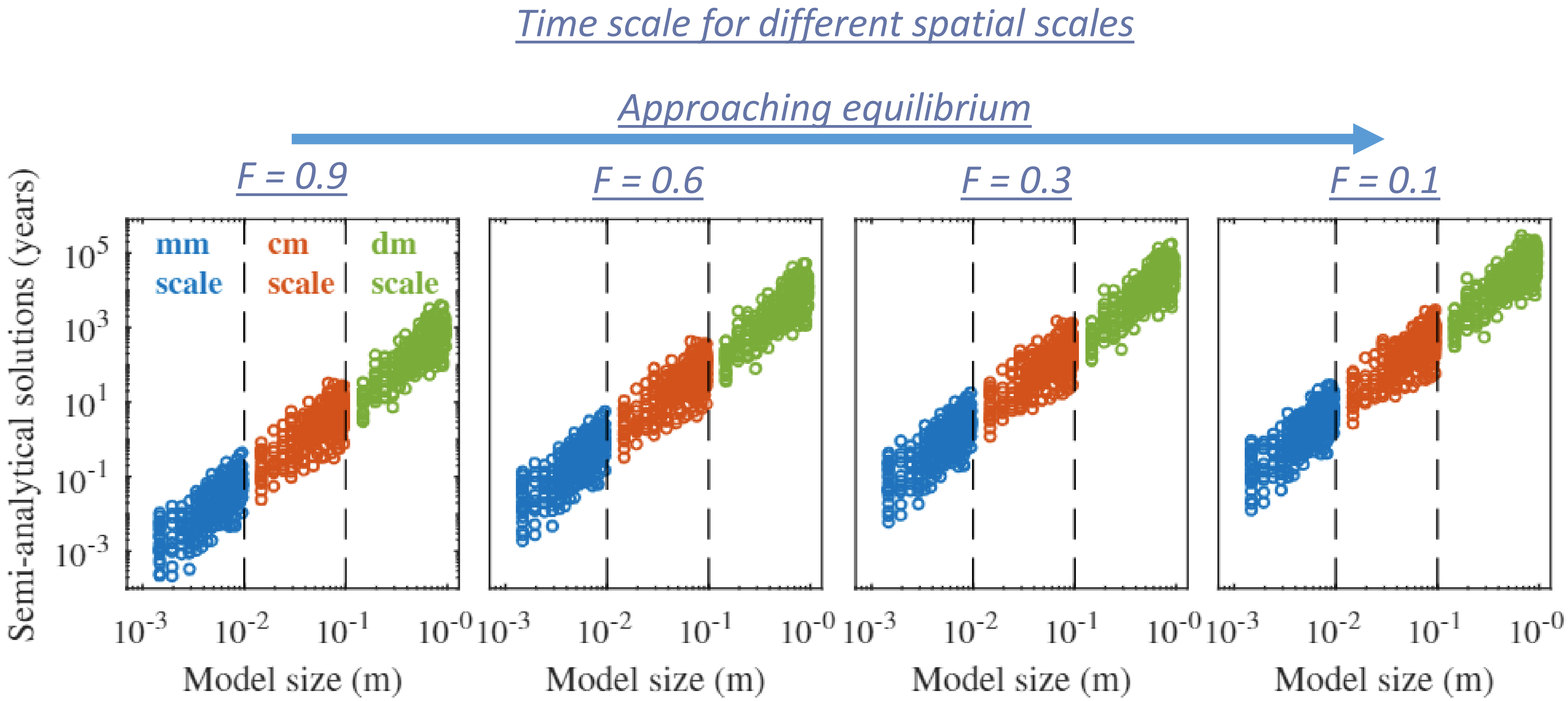

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- **How to find the time scale of residual CO_2 redistribution in heterogeneous systems?**
  - An approximate solution is derived to accurately predict the time scale at different stages before equilibrium for heterogeneous systems.
  - The impact of Ostwald ripening is more significant at small scales (days to years).

Thanks!