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# Reactive Transport

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# Objective

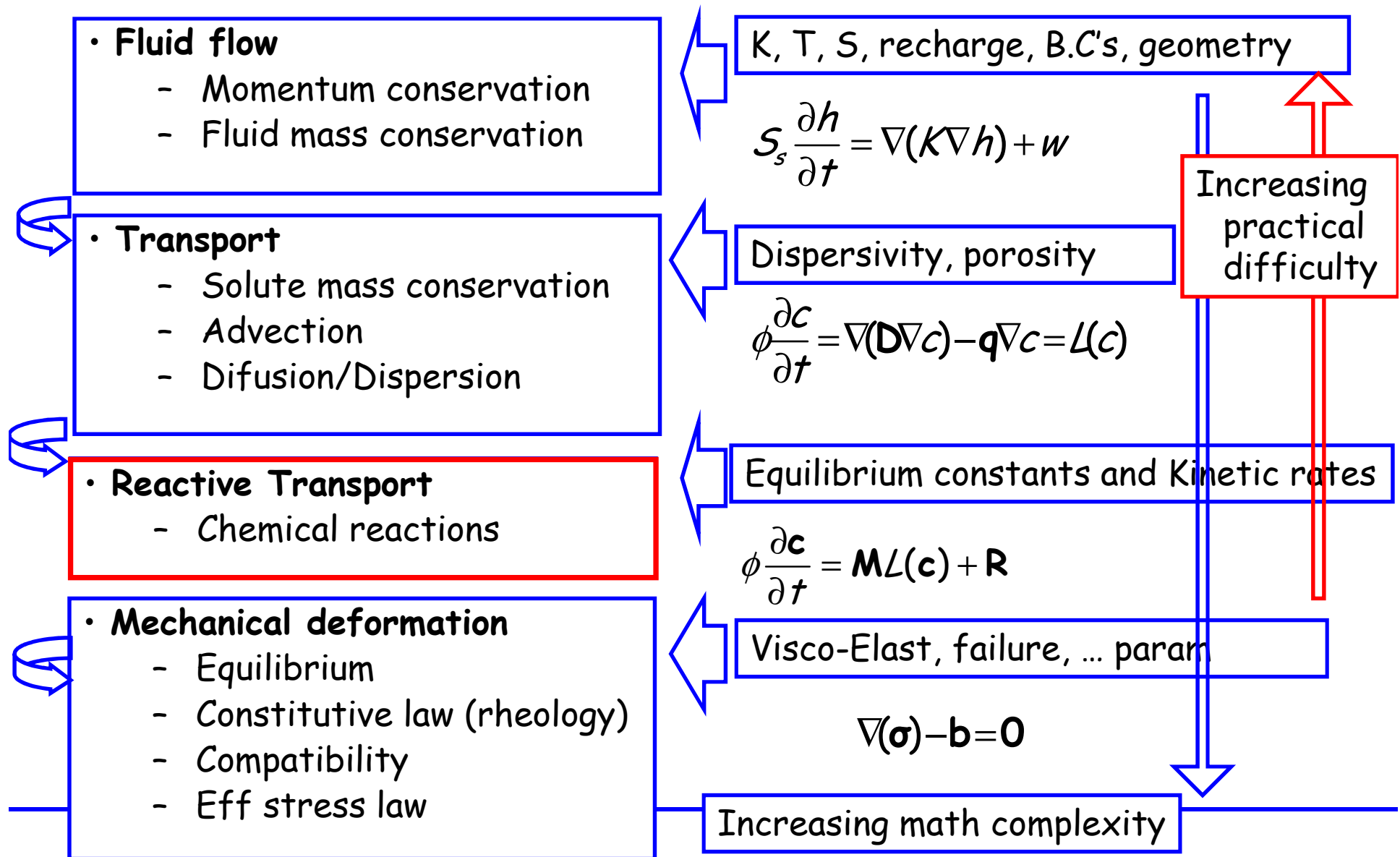
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- Motivate the need for Reactive transport
- Present a methodology to do it

## CONTENTS

- Background
  - Framing reactive transport
  - Types of problems: is it needed?
  - A bit of chemistry
- General approach
- Examples
- What about heterogeneity?

# Porous media ... and we are just starting...



# Summary (things you need to know)

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Reactive transport requires **two ingredients**

- 1) **Transport** (advection, dispersion, mixing, and all that)
  - 2) **Reactions**: many types, complex (**you need to work with someone who knows** the types of reactions we are going to work with), but conceptually easy
  - 3) We need **appropriate nomenclature** to work with these things (a **table** is a flat surface on which you can eat... or work... with 3 or four legs that separate it from the soil...)
-

# But, aren't there many reactions?

Indeed!

The technology of geochemistry is complex  
but not conceptually difficult

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# Ingredient 1: solute transport

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- Advection:  $\mathbf{v} = \mathbf{q}/\phi$  ( $\mathbf{q}$  proportional to  $\mathbf{K}$ )
- Dispersion: Proportional to:  $\alpha \mathbf{q}$
- Reactions
- Mass Conservation

$$\phi \frac{\partial c}{\partial t} = \nabla(\mathbf{D}\nabla c) - \mathbf{q}\nabla c + f - r$$

Porosity

Dispersion  
coeff.

Water  
flux

Reactions

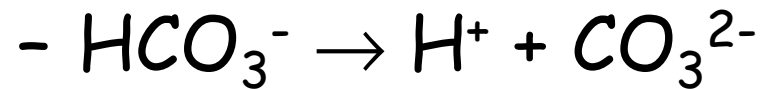
Written compactly

$$\mathcal{L}_t(c) = -\mathbf{q} \cdot \nabla c + \nabla \cdot (\mathbf{D}\nabla c)$$

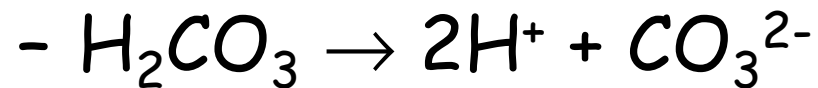


# To simplify chemistry, let us introduce matrix notation ...even better, vector space notation

- Traditional notation



$$K_1 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}}$$



$$K_2 = \frac{a_{\text{H}^+}^2 a_{\text{CO}_3^{2-}}}{a_{\text{H}_2\text{CO}_3}}$$

- Matrix notation

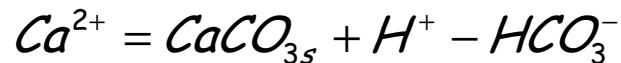
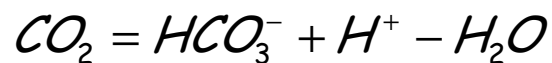
$$\mathbf{S}_e \log \mathbf{a} = \log \mathbf{K}$$

$$\begin{pmatrix} 1 & 1 & -1 & 0 \\ 2 & 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} \log a_{\text{H}^+} \\ \log a_{\text{CO}_3^{2-}} \\ \log a_{\text{HCO}_3^-} \\ \log a_{\text{H}_2\text{CO}_3} \end{pmatrix} = \begin{pmatrix} \log K_1 \\ \log K_2 \end{pmatrix}$$



# Ingredient 2: Chemical reactions: Stoichiometric matrix

- Assume a chemical system



Let  $r_i$  be the number of moles of reactants that evolve into products for the  $i$ -th reaction

- Stoichiometric Matrix (rows: reactions; columns: species)

$$\mathbf{S} = \left( \begin{array}{cc|cc|cc}
 \text{H}^+ & \text{HCO}_3^- & \text{CO}_3^{2-} & \text{CO}_2 & \text{Ca}^{2+} & \text{CaCO}_{3s} & \text{H}_2\text{O} \\
 -1 & 1 & -1 & 0 & 0 & 0 & 0 \\
 1 & 1 & 0 & -1 & 0 & 0 & -1 \\
 1 & -1 & 0 & 0 & -1 & 1 & 0
 \end{array} \right)$$

↔ Primary
↔ Secondary
↔ Constant Ac.

The columns of  $S$  can be viewed as the contribution of reactions to each species

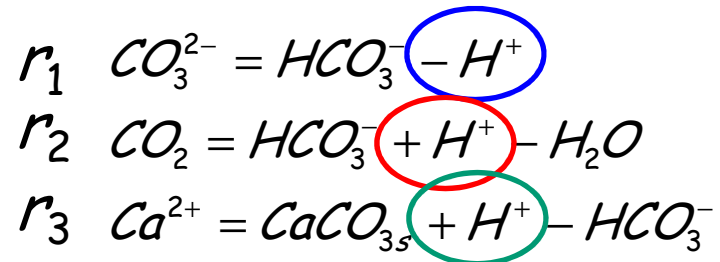
- Reaction rate: Mass balance

$$\mathbf{R} = \mathbf{S}^T \mathbf{r}$$

Contribution of reactions to the mass balance of each species

# Reactive transport

- Reactions



Let  $r_i$  be the number of moles of reactants that evolve into products for the  $i$ -th reaction

- Transport of all species

$$\begin{aligned}
 \phi \frac{\partial \text{H}^+}{\partial t} &= L(\text{H}^+) (-r_1 + r_2 + r_3) & \phi \frac{\partial \text{HCO}_3^-}{\partial t} &= L(\text{HCO}_3^-) + r_1 + r_2 - r_3 \\
 \phi \frac{\partial \text{CO}_3^{2-}}{\partial t} &= L(\text{CO}_3^{2-}) - r_1 & \phi \frac{\partial \text{CO}_2}{\partial t} &= L(\text{CO}_2) - r_2 & \phi \frac{\partial \text{Ca}^{2+}}{\partial t} &= L(\text{Ca}^{2+}) - r_3
 \end{aligned}$$

- Recall  $\mathbf{S}$

$$\mathbf{S} = \left( \begin{array}{cc|ccc|cc}
 \text{H}^+ & \text{HCO}_3^- & \text{CO}_3^{2-} & \text{CO}_2 & \text{Ca}^{2+} & \text{CaCO}_{3s} & \text{H}_2\text{O} \\
 -1 & 1 & -1 & 0 & 0 & 0 & 0 \\
 1 & 1 & 0 & -1 & 0 & 0 & -1 \\
 1 & -1 & 0 & 0 & -1 & 1 & 0
 \end{array} \right)$$

← Primary
← Secondary
← Constant Ac.

# Formulation of Reactive transport problems

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$$\frac{\partial \mathbf{c}}{\partial t} = \mathbf{M}L(\mathbf{c}) + \mathbf{S}_e^T \mathbf{r}_e + \mathbf{S}_k^T \mathbf{r}_k(\mathbf{c}) \quad n_s \text{ transport equations}$$

$$\left. \begin{array}{l} \mathbf{S}_{ea} \log \mathbf{c}_a = \log \mathbf{K} \\ \mathbf{r}_k = \mathbf{r}_k(\mathbf{c}) \end{array} \right\} n_r \text{ algebraic equations}$$

Looks awful! ( $n_r + n_s$  unknowns at every point)

Seek tricks and/or simplifications

And, thus, insight

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# So... objectives of this presentation

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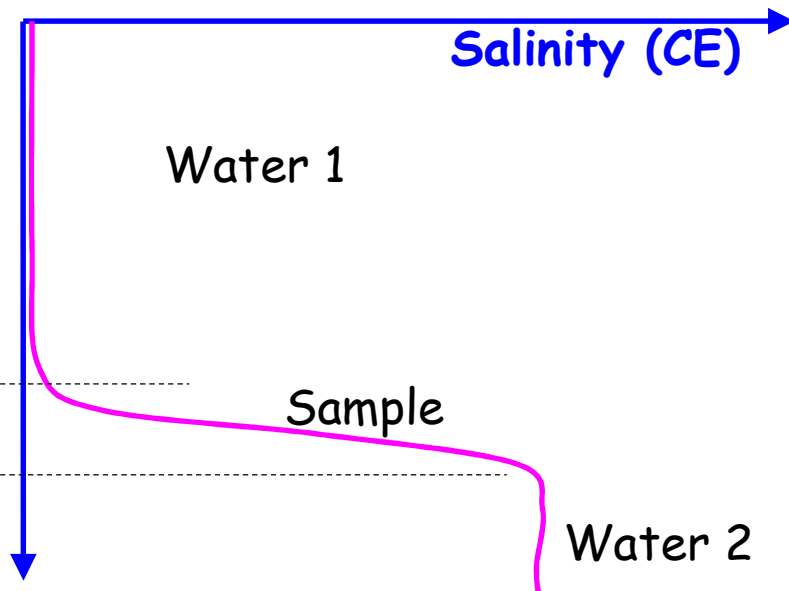
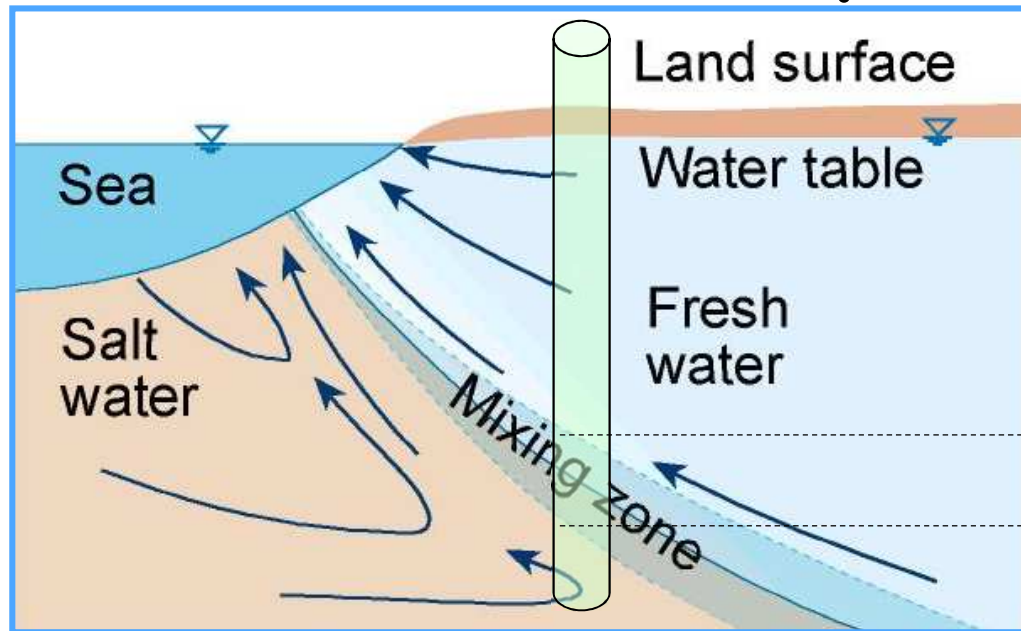
- Is reactive transport needed?
    - Wouldn't it be sufficient to find the residence time distribution to find out the total amount of reactions?
  - Can be understood?
  - Can be solved efficiently?

... and the answer is YES
  - Do we really know how to do it?

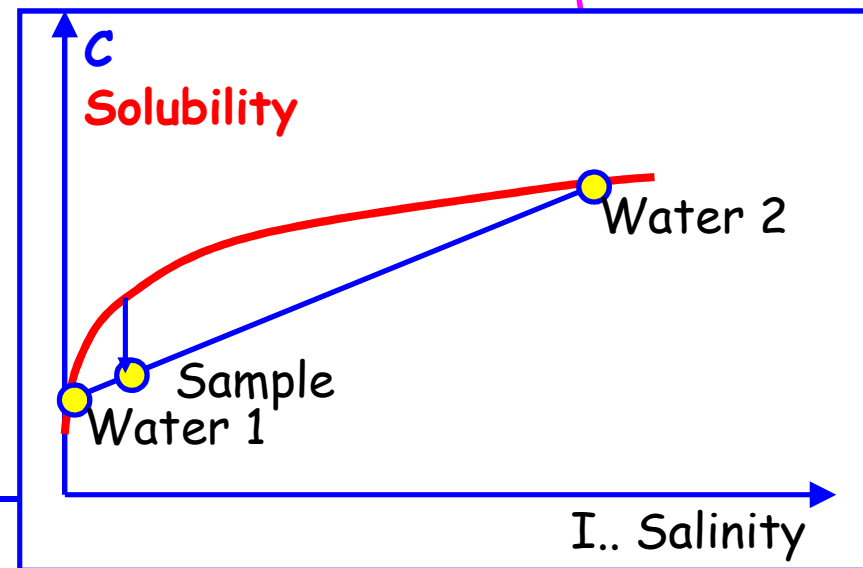
... not quite... but getting there  
... hopefully
-

# Why worry about reactive transport?

## Ex: Karst development in coastal areas

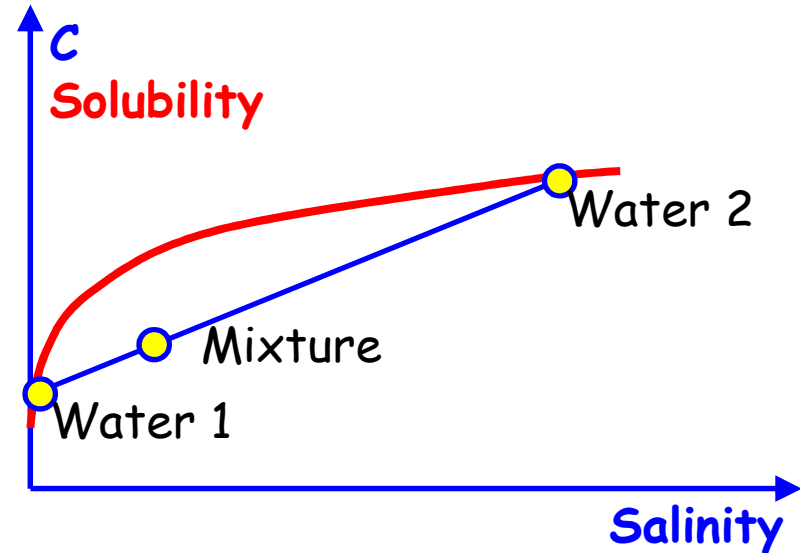


Waters 1 and 2 are in equilibrium. Yet, the mixture is undersaturated.



# Calcite dissolution in coastal aqf.

Mixture of two calcite saturated waters may be under or oversaturated with respect to calcite



To simulate this effect, consider 1D diffusion experiment

freshwater



saltwater

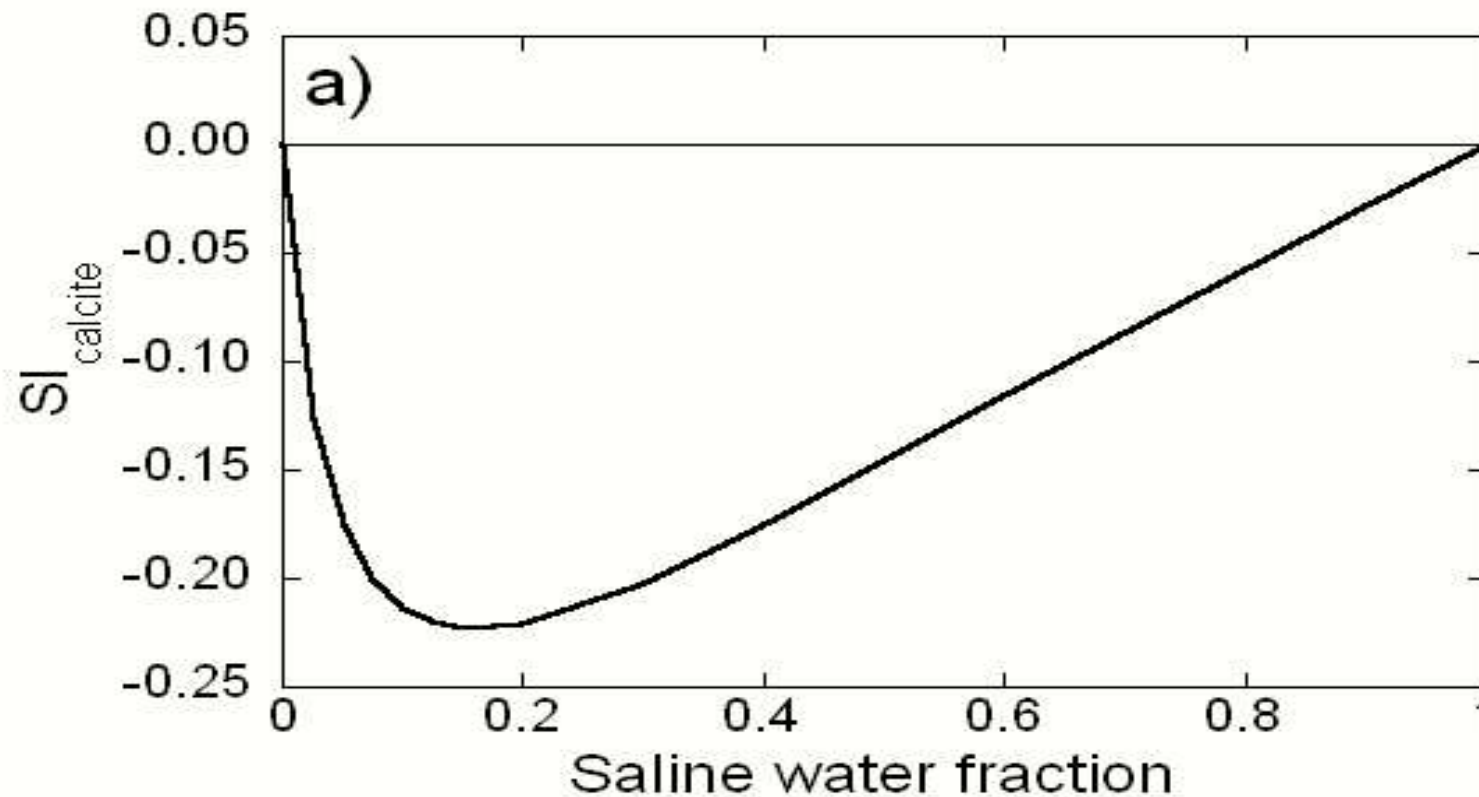
# Saturation Index

$$SI = \log \left( \frac{[CO_3^{2-}][Ca^{2+}]}{K_s} \right)$$

SI > 0    Oversaturated → Precipitation

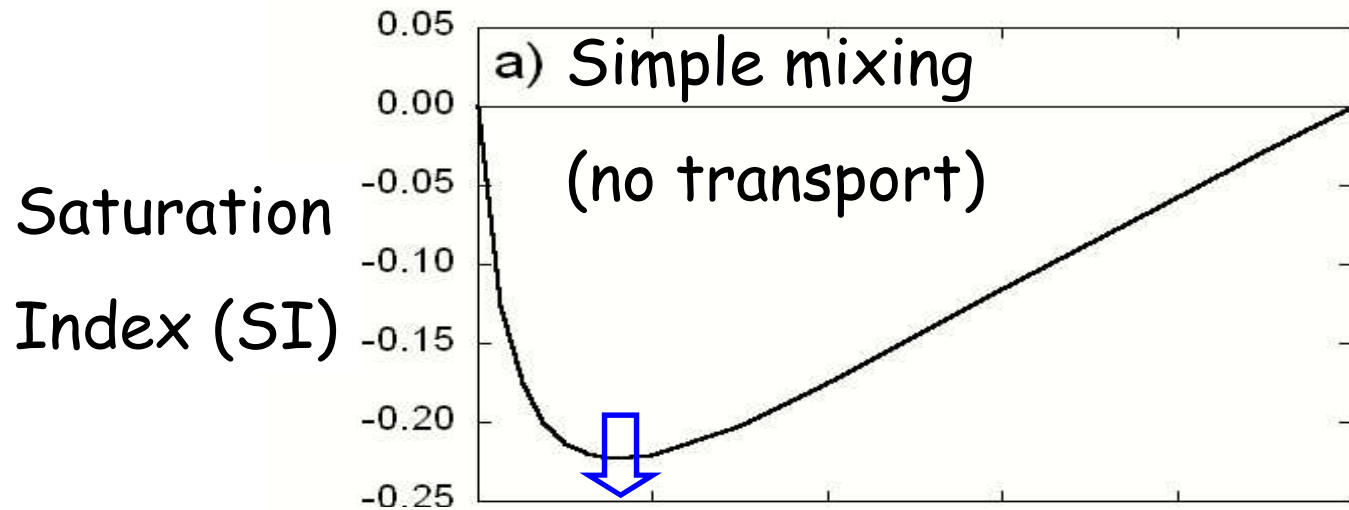
SI = 0    Equilibrium

SI < 0    Undersaturated → Dissolution

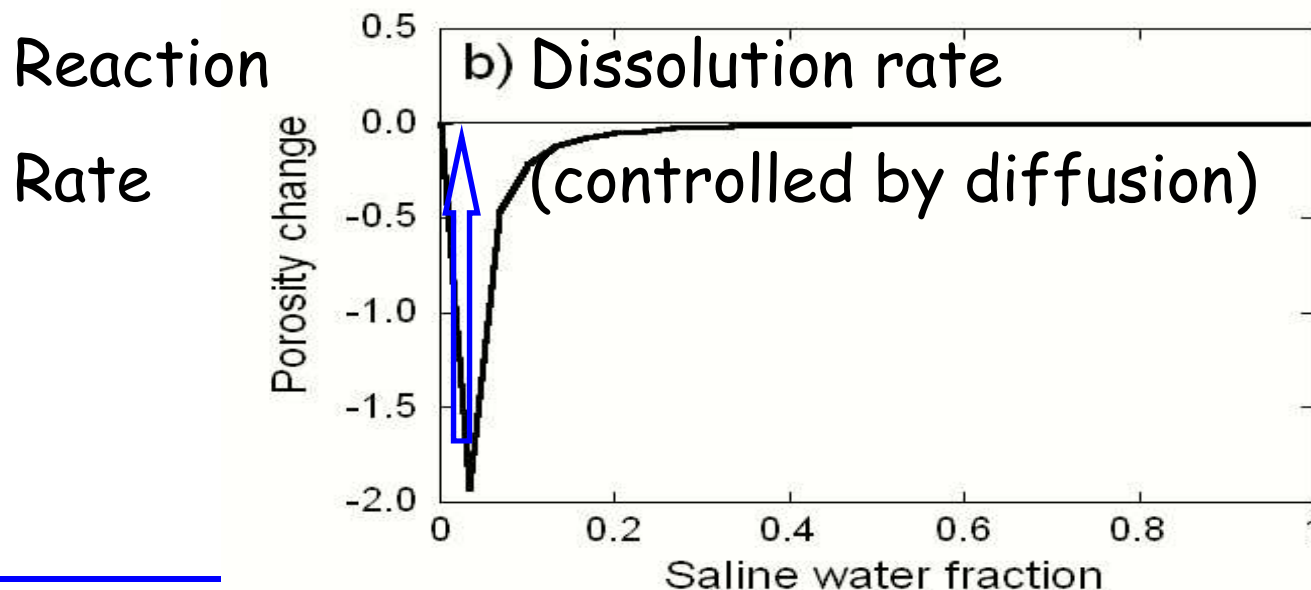




# SI & r

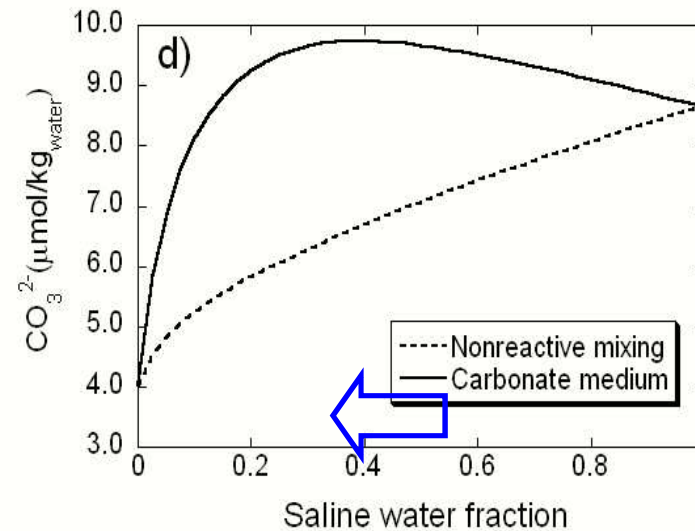
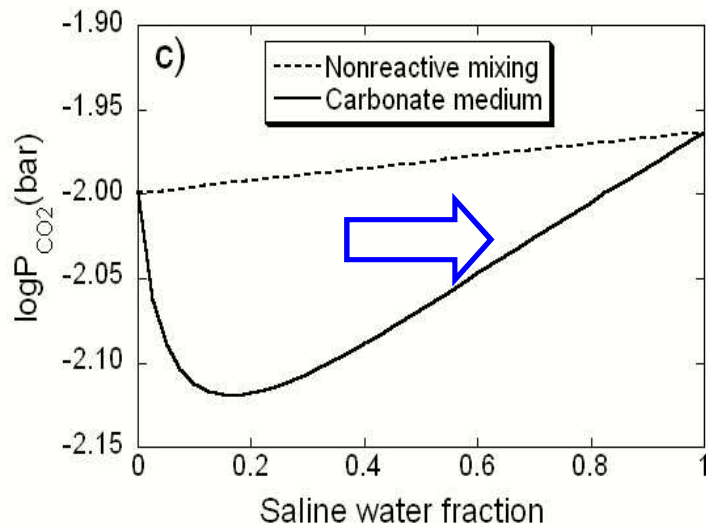
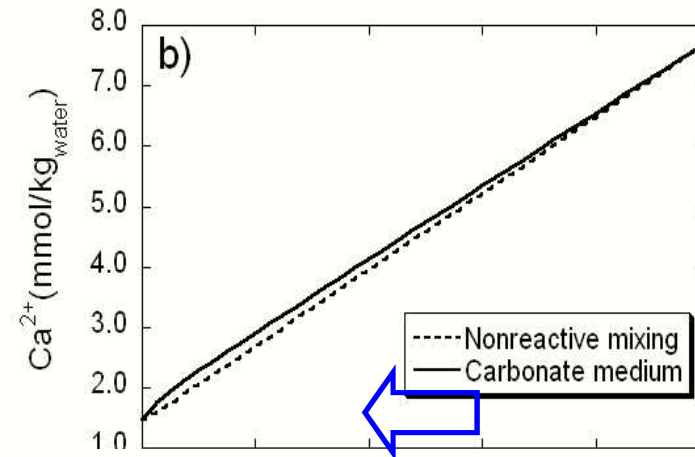
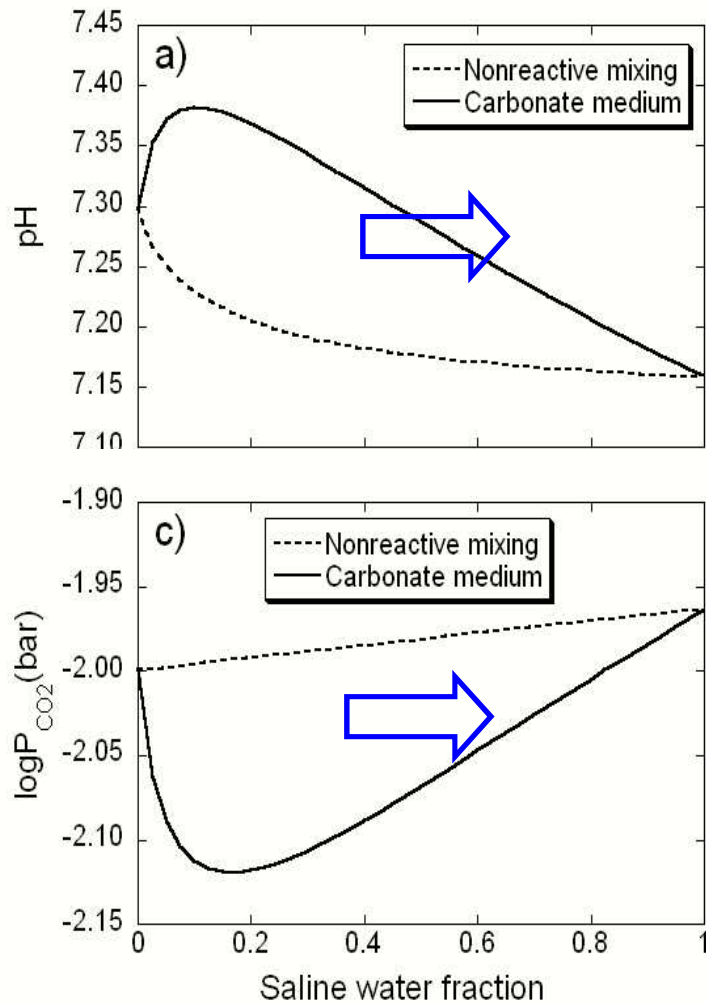


Mixing leads to maximum undersaturation for 20% fresh water and max. dissolution for 50% mixing



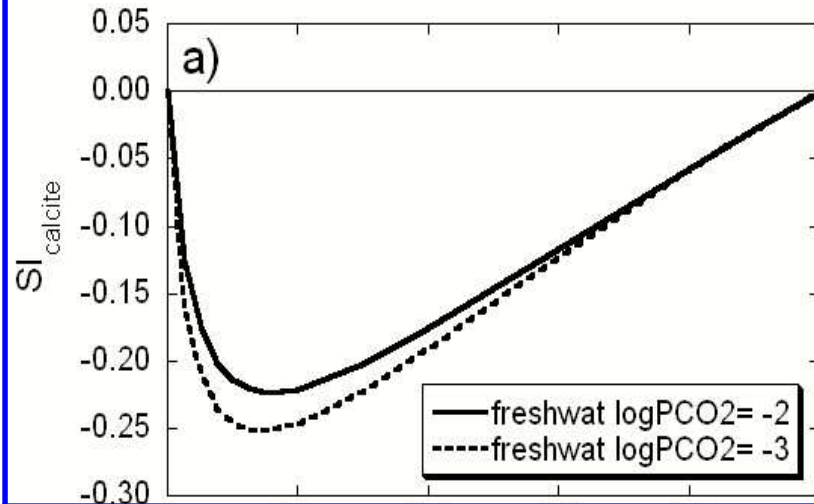
Dissolution rate proportional to Diff coeff. and maximum at the fresh water end

# Speciation

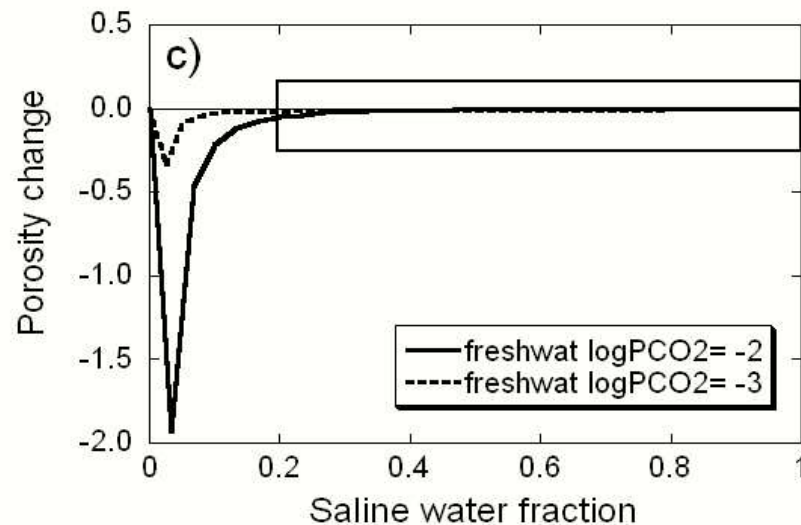


Dissolution causes diffusion of  $\text{CO}_2$  (acidity) at the freshwater end, which drives further dissolution

# Sensitivity to $CO_2$



Reducing concentration of  $CO_2$  at the freshwater end, causes an increase in subsaturation. Therefore, one would expect an increase in dissolution rate



However, dissolution rate is dramatically reduced

# First conclusion

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The interplay between transport and reactions is non-trivial.  
Saturation index calculations are needed but they fail to indicate

- 1) how much calcite is dissolved, which is controlled by mixing rate,
- 2) nor where (or under which conditions) dissolution rate is maximum.

Simulating reactive transport **is needed** to understand the fate of reacting solutes!

# Still, isn't it too difficult?

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- Yes, if using brute force
  - However, a number of "tricks" are possible, depending on the type of chemical system
    - If all reactions in equilibrium (Desimoni et al, 2005)
    - If also kinetic reactions (Molins et al, 2007)
    - In general (Saaltink et al, 1998)
-

# The basic trick: components

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$$\frac{\partial \mathbf{c}}{\partial t} = \mathbf{M}L(\mathbf{c}) + \mathbf{S}_e^T \mathbf{r}_e + \mathbf{S}_k^T \mathbf{r}_k(\mathbf{c})$$

Choose component matrix  $\mathbf{U}$ , such that

$$\mathbf{U}\mathbf{S}_e^T = \mathbf{0} \Rightarrow \mathbf{U}\mathbf{S}_e^T \mathbf{r}_e = \mathbf{0}$$

Then,

$$\mathbf{U} \frac{\partial \mathbf{c}}{\partial t} = \mathbf{U}\mathbf{M}L(\mathbf{c}) + \mathbf{U}\mathbf{S}_k^T \mathbf{r}_k(\mathbf{c})$$

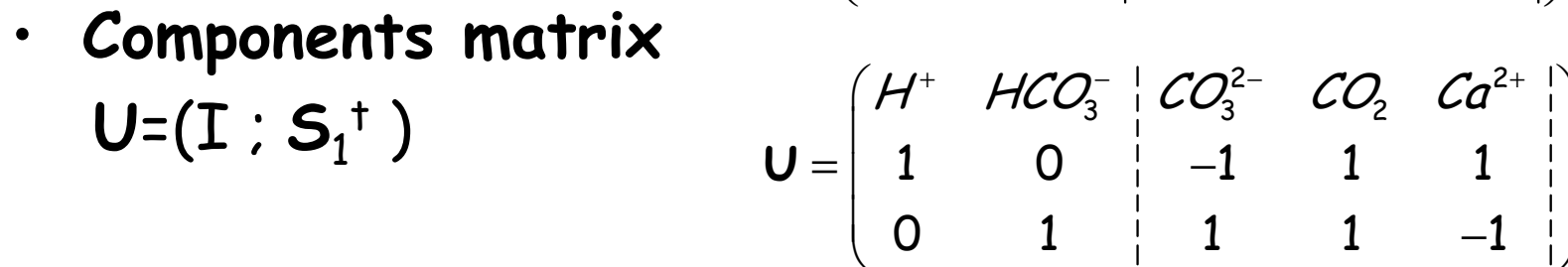
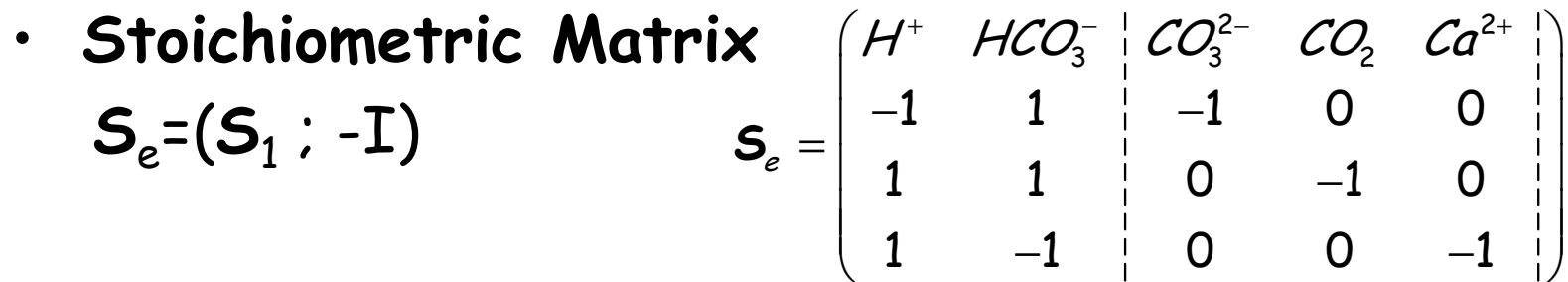
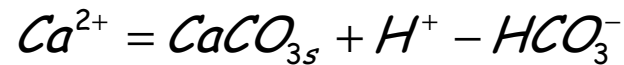
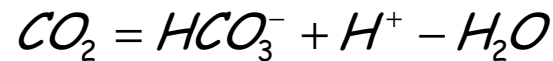
Components:  $\mathbf{u} = \mathbf{U}\mathbf{c}$

Linear combinations of species that remain unaltered by equilibrium reactions

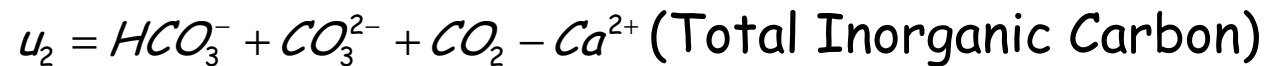
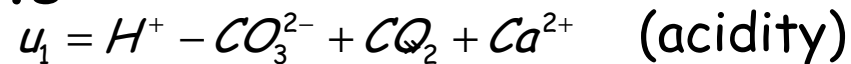
$n_s - n_r$  transport equations.

(A good choice of  $\mathbf{U}$  allows to decouple (some of) these equations!)

# Example



- **Components**





# Role of components

$$\phi \frac{\partial H^+}{\partial t} = L(H^+) - r_1 + r_2 + r_3$$

$$\phi \frac{\partial HCO_3^-}{\partial t} = L(HCO_3^-) + r_1 + r_2 - r_3$$

$$\phi \frac{\partial CO_3^{2-}}{\partial t} = L(CO_3^{2-}) - r_1$$

$$\phi \frac{\partial CO_2}{\partial t} = L(CO_2) - r_2$$

$$\phi \frac{\partial Ca^{2+}}{\partial t} = L(Ca^{2+}) - r_3$$

$$u_1 = H^+ - CO_3^{2-} + CO_2 + Ca^{2+}$$

$$u_2 = HCO_3^- + CO_3^{2-} + CO_2 - Ca^{2+}$$

$$U = \left( \begin{array}{cc|ccc} H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Ca^{2+} \\ 1 & 0 & -1 & 1 & 1 \\ 0 & 1 & 1 & 1 & -1 \end{array} \right)$$

Components are linear combinations of species such that equilibrium  $r$ 's cancel out, so that 
$$\phi \frac{\partial u_1}{\partial t} = L(u_1)$$

# Procedure

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1. Define **chemical system** and components
  2. Solve transport equations for **components** (and/or primary species)
  3. **Speciation**: Compute species concentrations from components (and/or primary species)
  4. Substitute species back into transport equations to obtain **reaction rates**
-

# Analytical solution for 2 species

Assume 2 species (e.g.  $SO_4^{2-}$  and  $Ca^{2+}$ ) in eq. with gypsum

## Step 1: Chemical system



Stoichiometric matrix  $S_e = (-1 \quad -1 \quad 1)$

Components:  $U = (1 \quad -1) \Rightarrow u = [Ca^{2+}] - [SO_4^{2-}]$  is conservative!

## Step 2: Solve transport of $u$

Transport equations

where  $L_\tau(c) = -\mathbf{q} \cdot \nabla c + \nabla \cdot (\mathbf{D} \nabla c)$

$$\frac{\partial(\phi C_1)}{\partial t} - L_\tau(C_1) = -r \quad (1)$$

$$\frac{\partial(\phi C_2)}{\partial t} - L_\tau(C_2) = -r \quad (2)$$

(1)-(2) yields:  $\frac{\partial(\phi u)}{\partial t} = L_\tau(u)$

# Analytical solution for 2 species

## Step 3: Speciation

Solve  $u = C_1 - C_2$   
 Together with  $C_1 \cdot C_2 = K$  }  $\Rightarrow$

$$C_1 = \frac{u + \sqrt{u^2 + 4K}}{2}$$

$$C_2 = \frac{-u + \sqrt{u^2 + 4K}}{2} = C_2(u)$$

## Step 4: Compute r

Plugging  $C_2$  into  $\frac{\partial(\phi C_2)}{\partial t} - L(C_2) = -r$      $L(c) = -\mathbf{q} \cdot \nabla c + \nabla \cdot (\mathbf{D} \nabla c)$

We obtain

$$r = \frac{\partial^2 C_2}{\partial u^2} [\nabla u^T \cdot \mathbf{D} \cdot \nabla u]$$

Transport

Chemistry

$$\frac{\partial^2 C_2}{\partial u^2} = \frac{2K}{(u^2 + 4K)^{3/2}}$$

# Mixing of several waters

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## Step 3: Speciation

Can be very complex, but  $C_2 = C_2(\alpha)$

Where  $\alpha$  is the mixing ratio (possibly a vector)

## Step 4: Compute $r$

Plugging  $C_2$  into  $\frac{\partial(\phi C_2)}{\partial t} - L_1(C_2) =$

We obtain

$$r = \frac{\partial^2 C_2}{\partial \alpha^2} [\nabla \alpha^T \cdot \mathbf{D} \cdot \nabla \alpha]$$

That is,

1) Transport  $\alpha$

2) Use any code (e.g., PHREEQE, RETRASO,...) to compute speciation

# Mixing rate controls (fast) reactions

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- Mixing controls fast chemical reactions

(de Simoni et al, 2005, 2007; Valocchi & Cirpka, 2007)

- In fact, reaction rate of equilibrium reactions

$$r = \mathbf{H} \nabla^T c \cdot \mathbf{D} \cdot \nabla c = f_Q \cdot f_m$$

- Natural choice for (local) mixing rate

$$f_m = \nabla^T c \cdot \mathbf{D} \cdot \nabla c$$

(de Simoni et al, 2005, 2007; Kitanidis, 1994)

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## 2nd Conclusion

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**In the case of aqueous and dissolution-precipitation reactions in equilibrium:**

1. Reactive Transport is indeed easy!
2. Only need to solve for independent components. In the calcite example: 2 components are needed (+salinity)...  
Actually, it suffices to work with mixing ratios... (Desimoni et al., 2007). And, now, not even that (just mixing rates!)

**3. Mixing drives fast reactions**

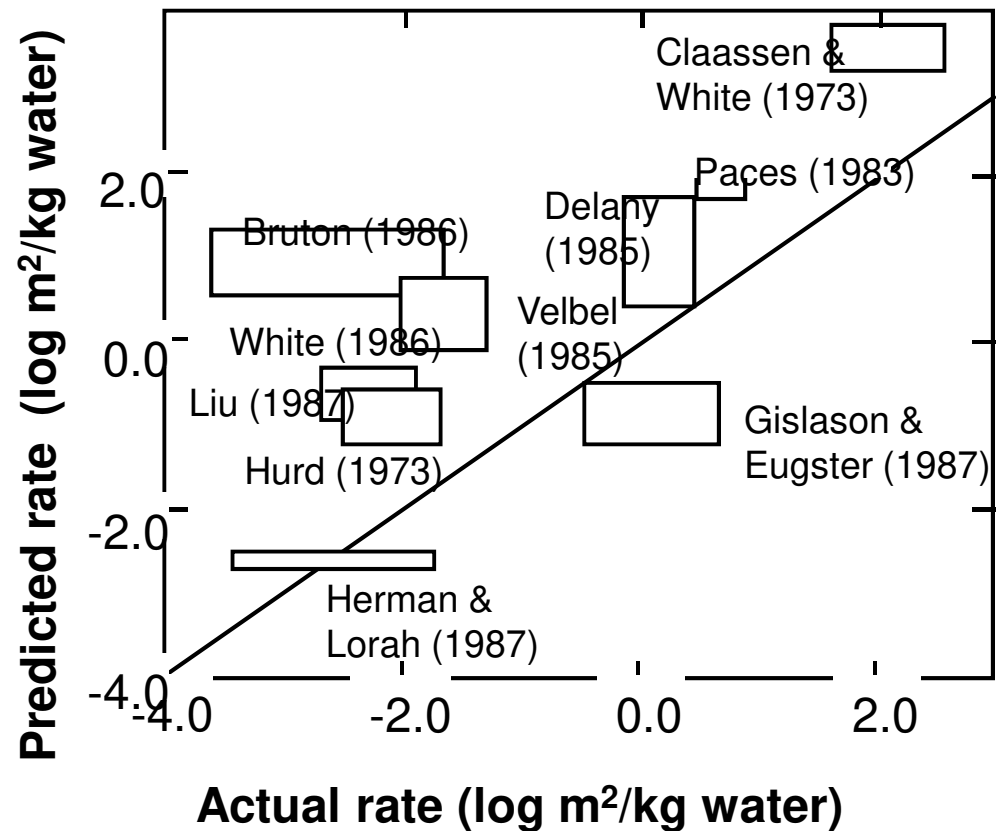
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# Does it work?

- ~~Slower than predicted reaction rates~~

Far slower than predicted reaction rates



(White & Peterson, 1990)

# But do we know how to represent mixing? Does dispersion represent mixing?

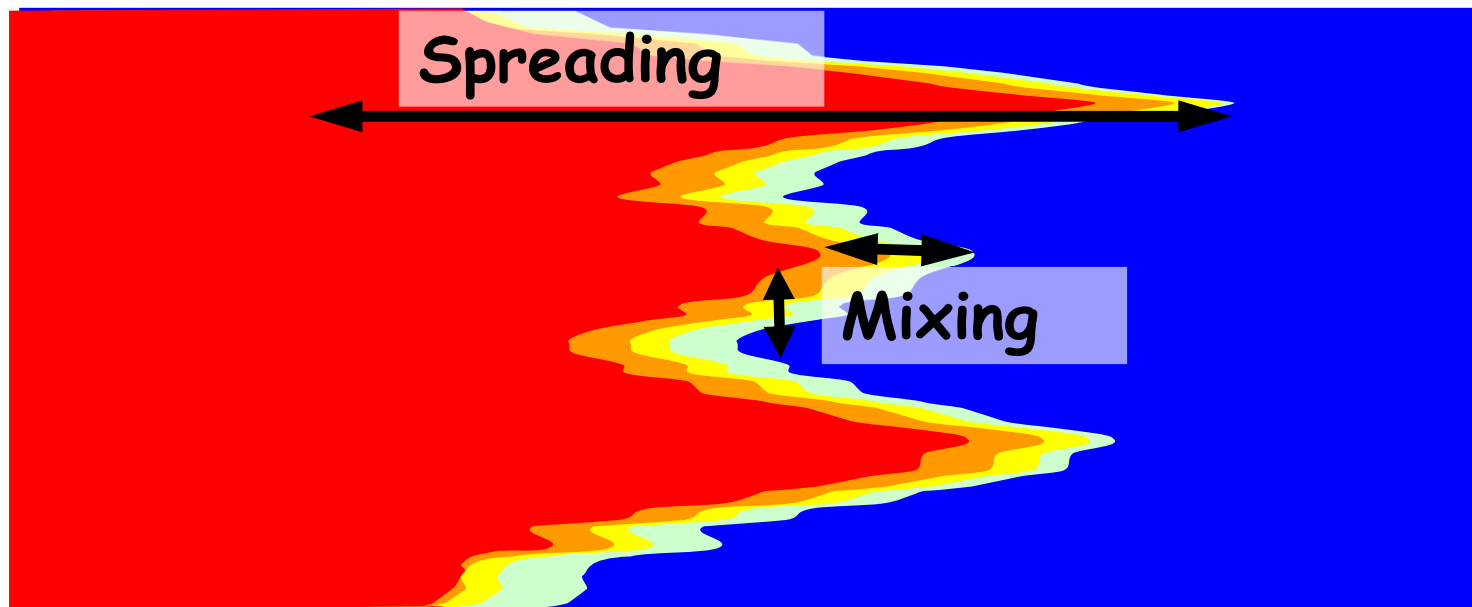
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Dispersion = the rate of growth of plumes

Therefore Dispersion=spreading rate

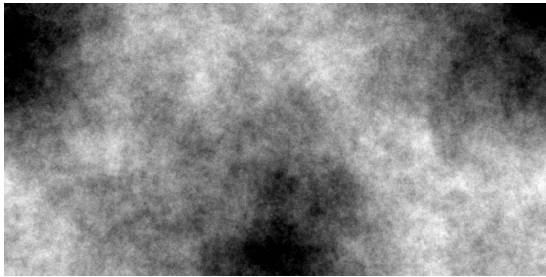
Mixing reflects local gradients (internal disorder within a plume)

$$D = \frac{1}{2} \frac{\partial \sigma_{ii}^2}{\partial t}$$



# Non-local (in t) formulations for RT

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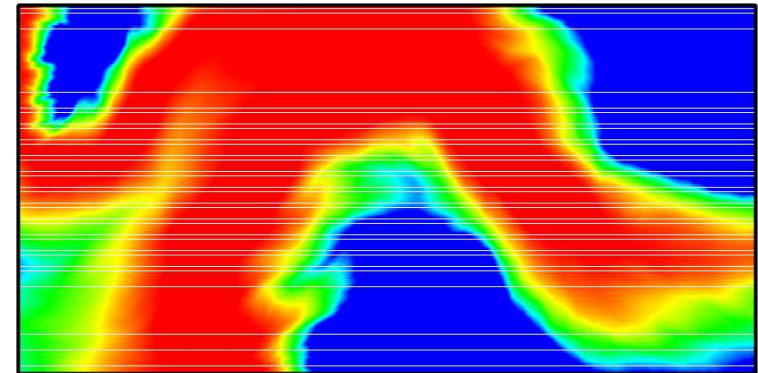
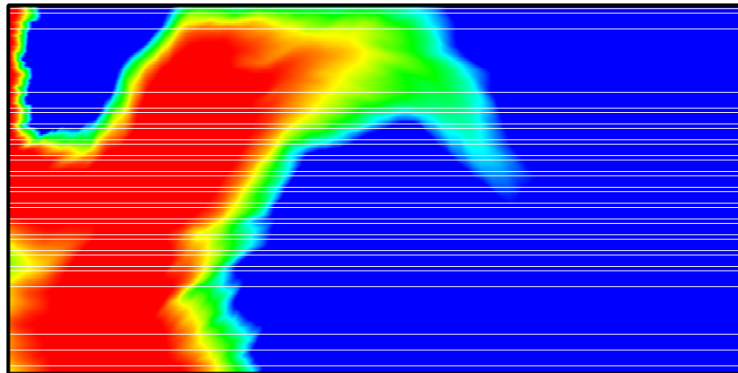


Willmann et al (WRR, 2010) simulated RT through heterogeneous medium

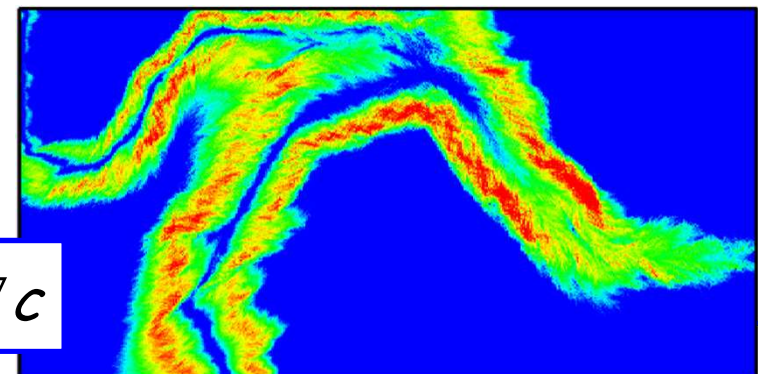
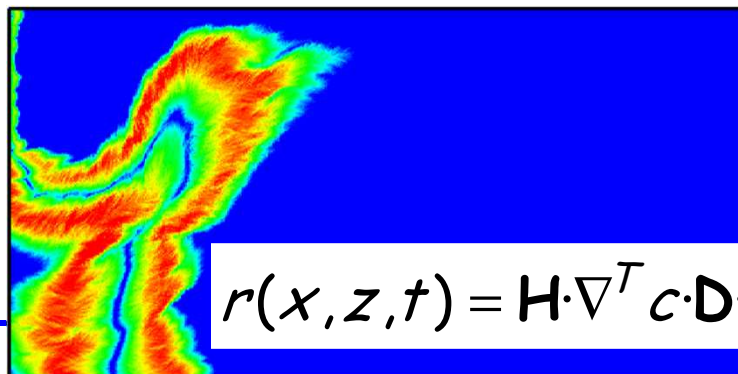
time 1

time 2

Conservative  
Component



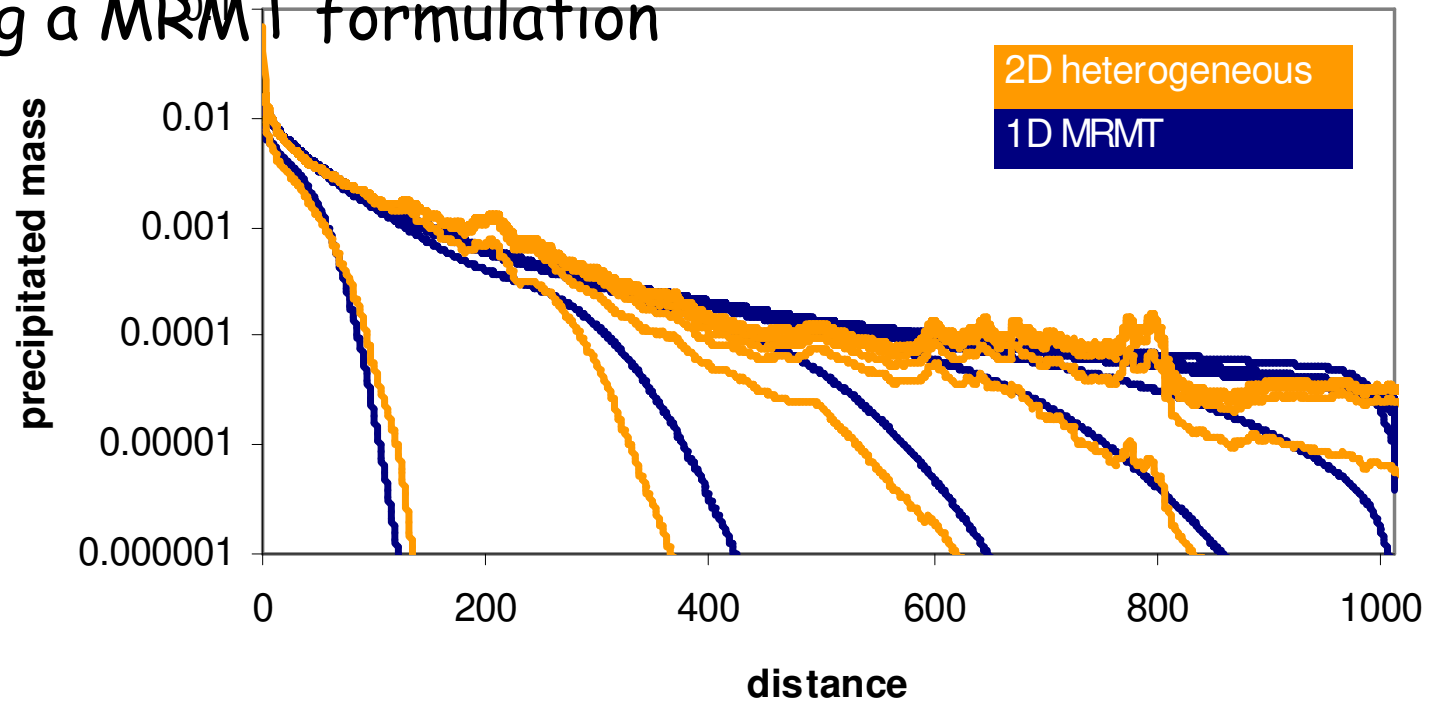
reaction  
rates



$$r(x, z, t) = H \cdot \nabla^T c \cdot D \cdot \nabla c$$

# Non-local (in t) formulations for RT

Willmann et al (WRR, 2010) predicted quite accurately the overall (integrated in t and z) reaction rate, and thus mixing using a MRMT formulation



Non-local formulations reproduce mixing, but Willman required a tracer test to characterize memory function, can it be defined from site characterization?

# Conclusion 2

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- Non-local formulations reproduce
  - Scale dependence of dispersion (spreading)
  - Scale dependence of apparent porosity
  - Tailing
  - Not too bad for reaction rates (mixing)
  - and easy to implement in existing codes!

- **Mixing is the critical issue, but:**
    - Can mixing be defined from geological characterization?
    - **Is it true that mixing well represented by MRMT?**
-

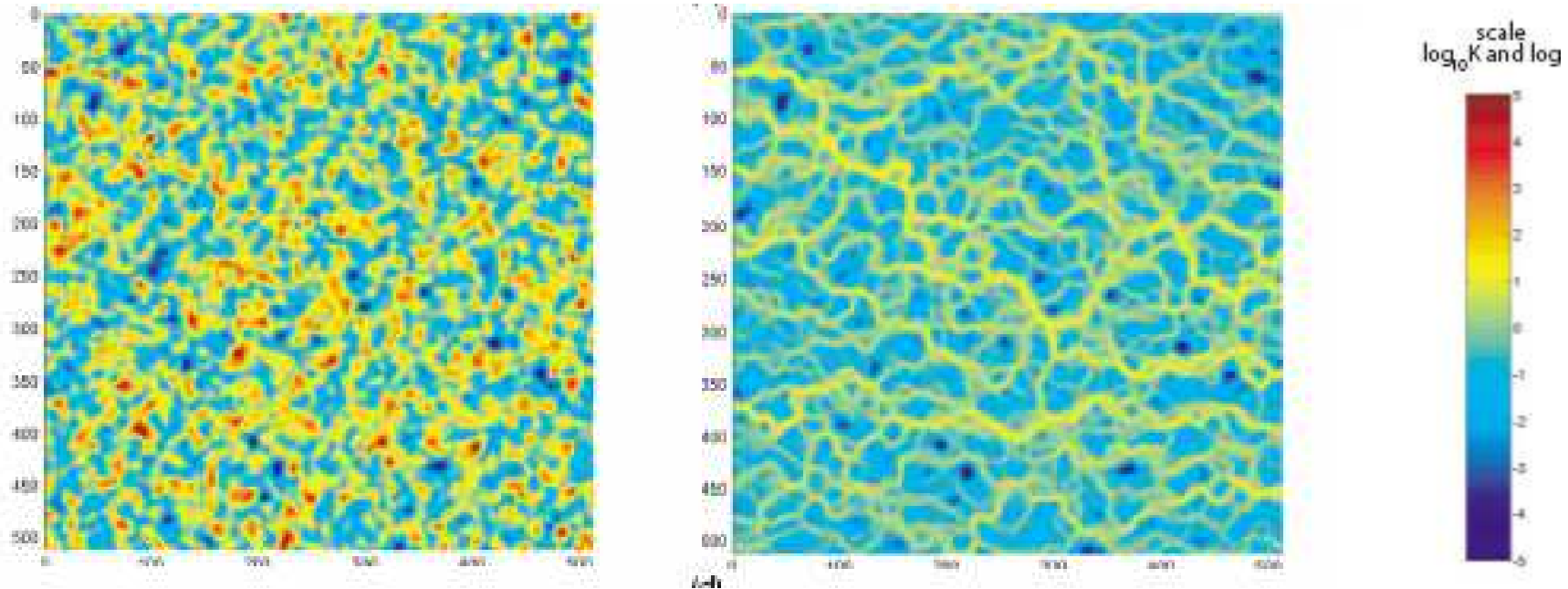
# OBJECTIVE

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- Test validity of MRMT
  - First, separate mixing from spreading
  - Second, select right memory function

# Numerical simulations of mixing in heterogeneous porous media

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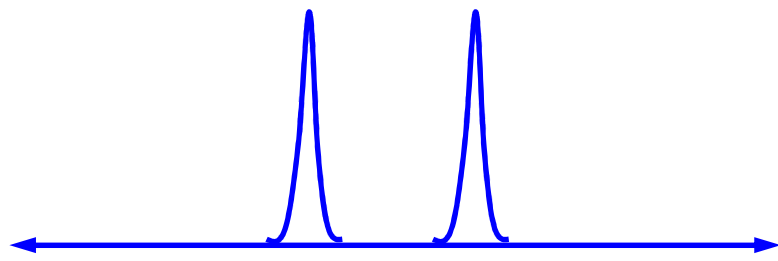
- Multi-lognormal permeability fields
- Log permeability field variance  $s^2_{\ln K}$
- Gaussian correlation function
- Correlation length  $\lambda=10$
- Permeater boundary conditions
- Steady flow

- Initial line injection
- Domain size 512x8192
- Local advection-diffusion
- Peclet number:

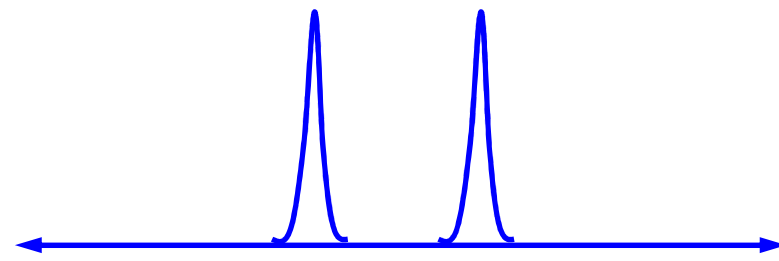
$$Pe = \frac{\lambda \overline{v \nabla h}}{D} = 10^2 - 10^3$$



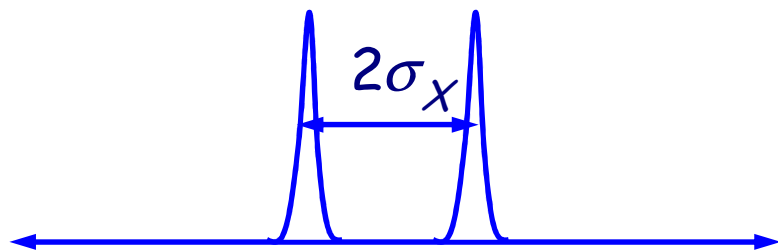
# Differentiating mixing and dispersion



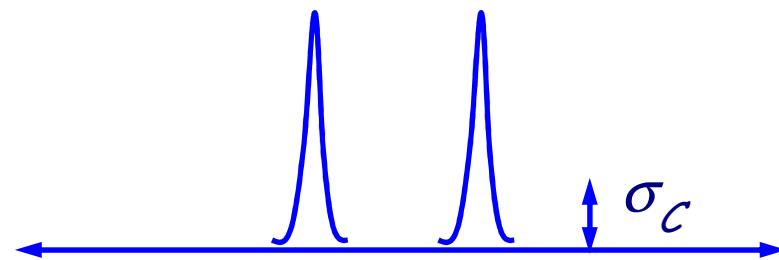
Pure dispersion



Pure mixing



Spreading, but no dilution

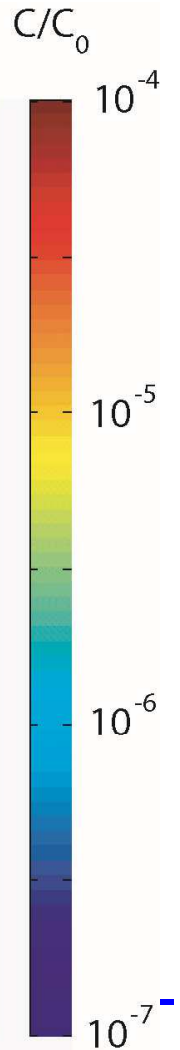
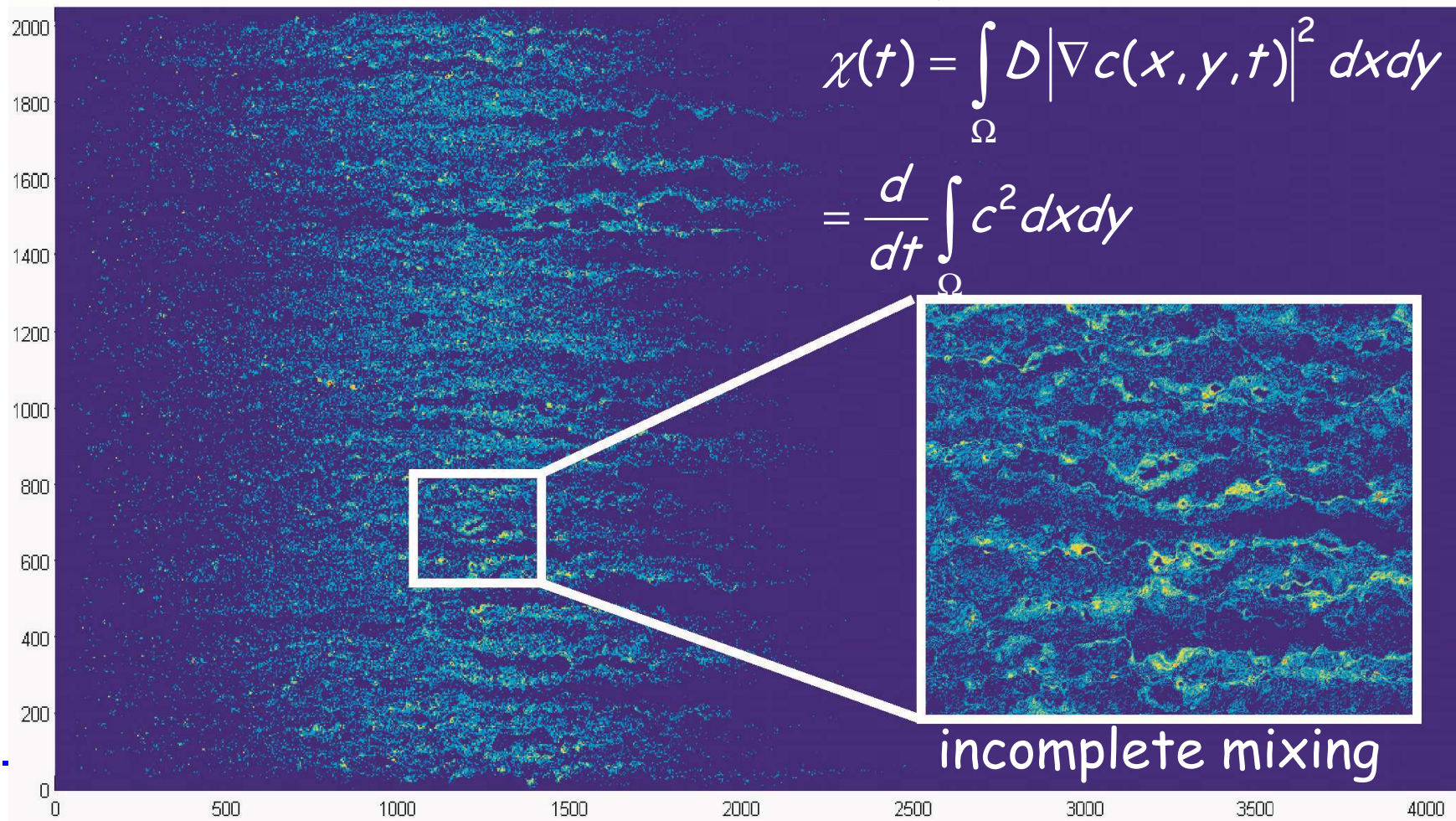


Dilution, but no spreading

# Global mixing and spreading

Spreading  
(characterized by  $\sigma_x$ )

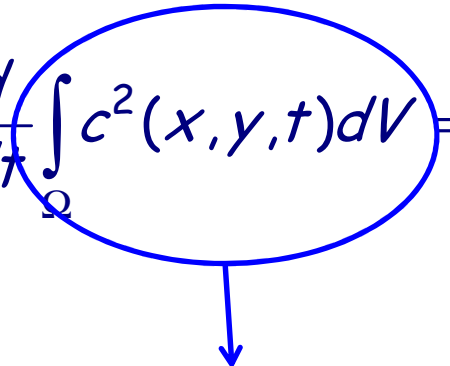
Mixing characterized  
by global mixing rate



# Use dissipation rate to compute overall mixing

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Overall mixing rate

$$\chi(t) = \int_{\Omega} \nabla c(x, y, t) \cdot D \cdot \nabla c(x, y, t) dV = \frac{1}{2} \frac{d}{dt} \int_{\Omega} c^2(x, y, t) dV = \frac{1}{2} \frac{d}{dt} M_2$$


Mixing state

Separate mixing rate (and state) into macrodispersion driven (reference) and internal disorder driven

---

# Separating mixing and spreading?

1. Decompose  $c$ :

$$c = \bar{c} + c'$$

2. Vertical averaging

$$\bar{c}(x,t) = \frac{1}{L_y} \int_0^{L_y} c(x,y,t) dy$$

3. Compute variance of averaged concentration (reference mixing state, controlled by macrodispersion)

$$M_1(t) = \int_0^{L_x} \bar{c}^2 dx \quad M_G = \frac{m_0^2}{2L_2 \sqrt{\pi \sigma_L}}$$

4. Compute "internal mixing" (caused by internal disorder):

$$M_2(t) = \int_{\Omega} (c')^2 dV$$

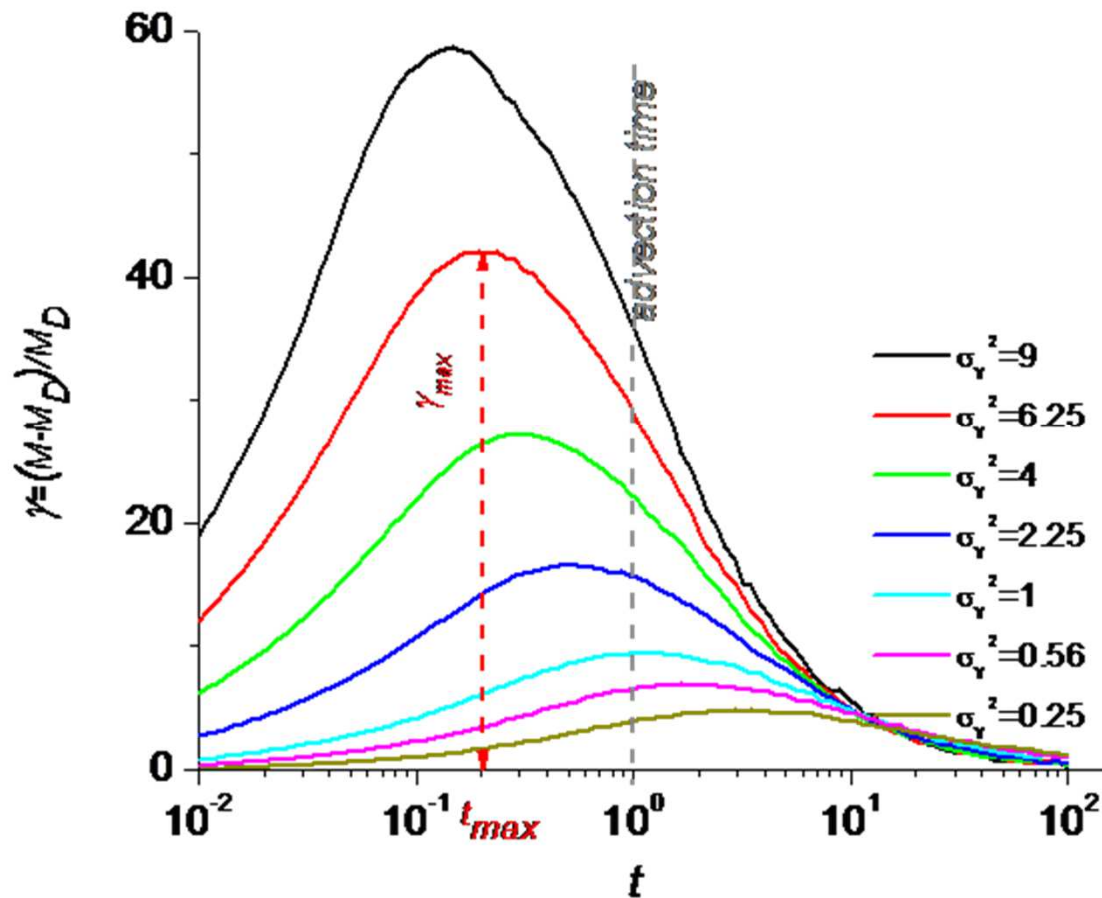
# Separating mixing and spreading?

$$M_1(t) = \int_0^{Lx} \bar{c}^2 dx \quad M_G = \frac{m_0^2}{2L_2 \sqrt{\pi\sigma_L}} \quad M_2(t) = \int_{\Omega} (c')^2 dV$$

1. Clearly:  $M(t) = \int_{\Omega} c^2 dx \quad M_G + M_2$
2. Therefore, it is natural to measure "internal disorder" by:

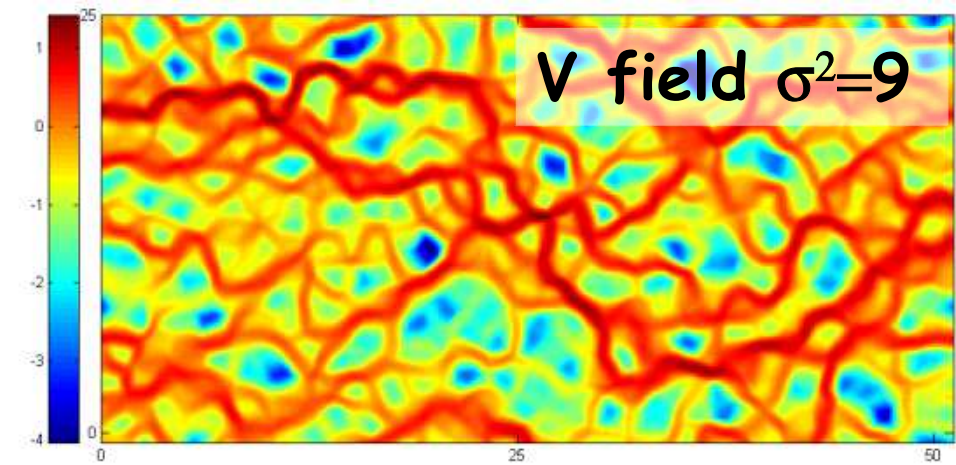
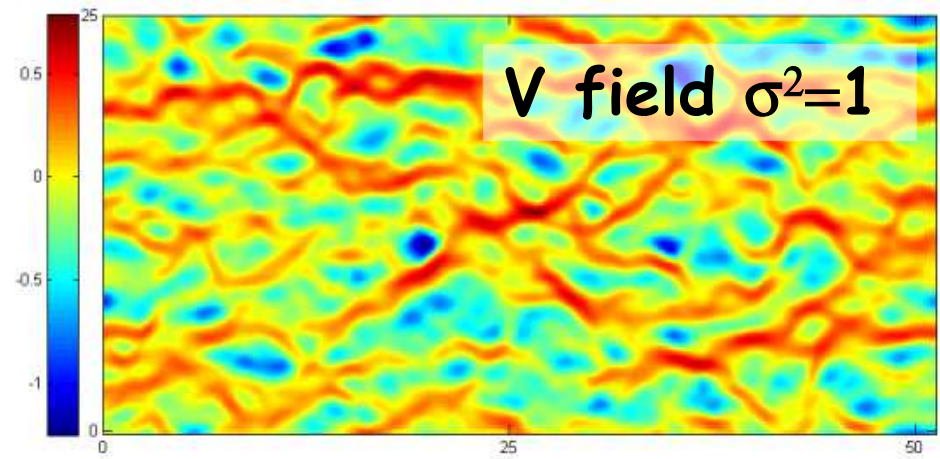
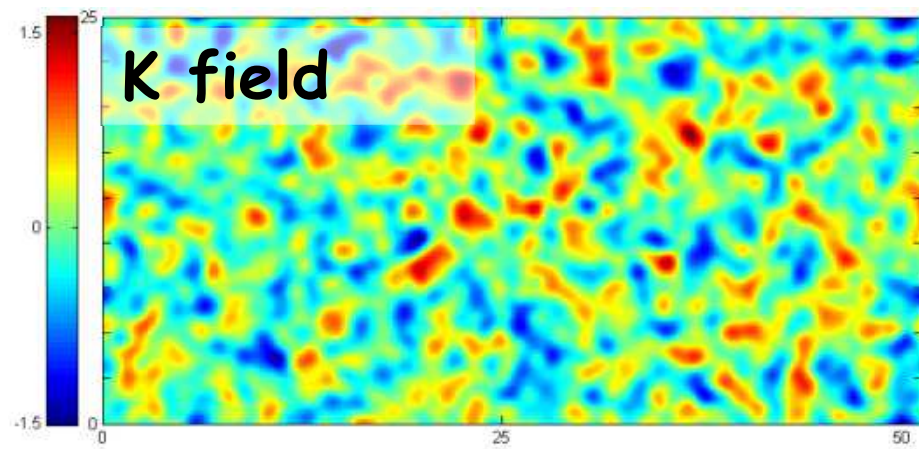
$$\gamma(t) = \frac{M_2(t)}{M_G(t)} = \frac{M(t) - M_G(t)}{M_G(t)}$$

# Characterizing the $\gamma$ function



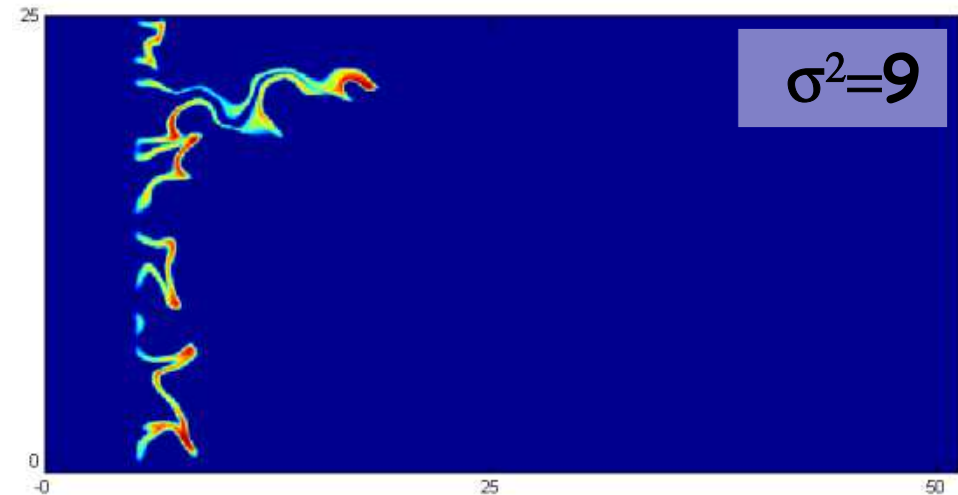
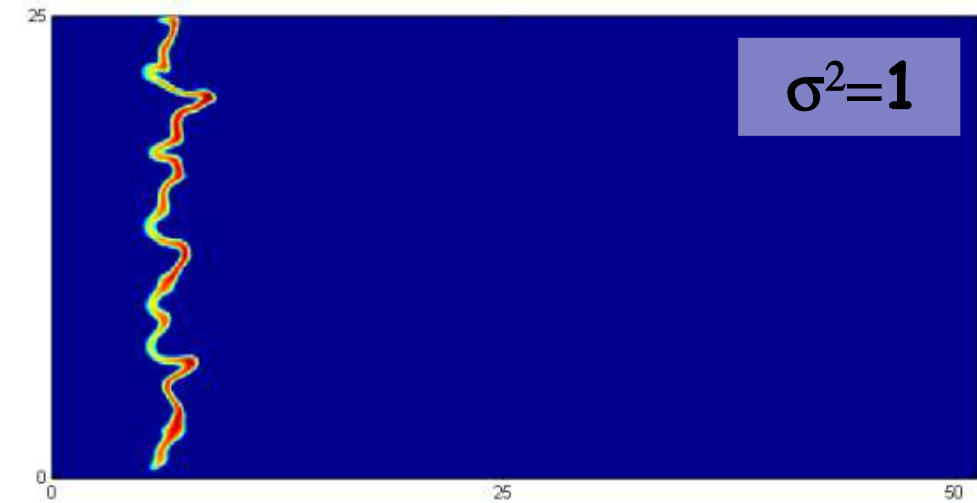
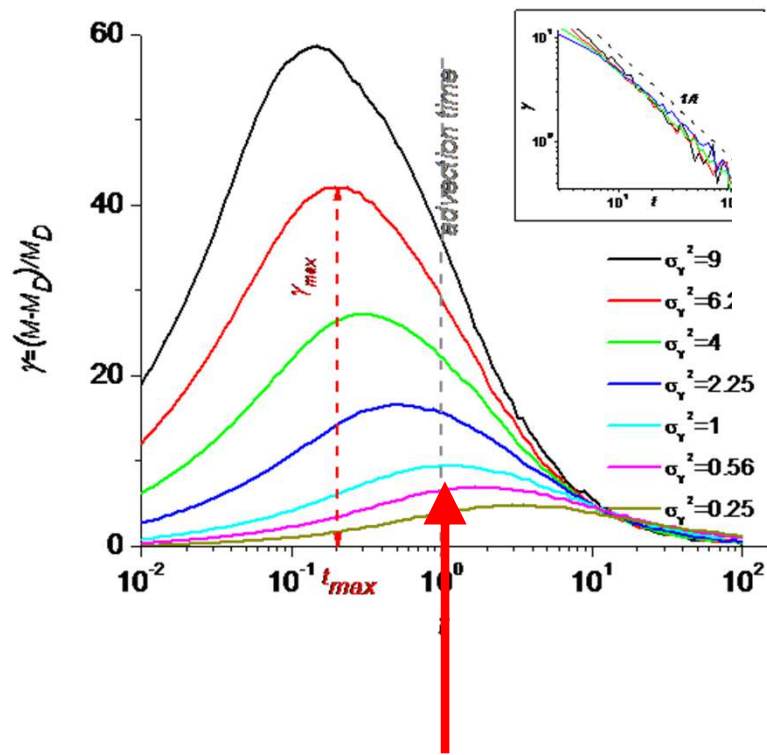
Mixing and spreading  
identical at late times  
(even though not fully  
mixed)





# understanding the $\gamma$ function

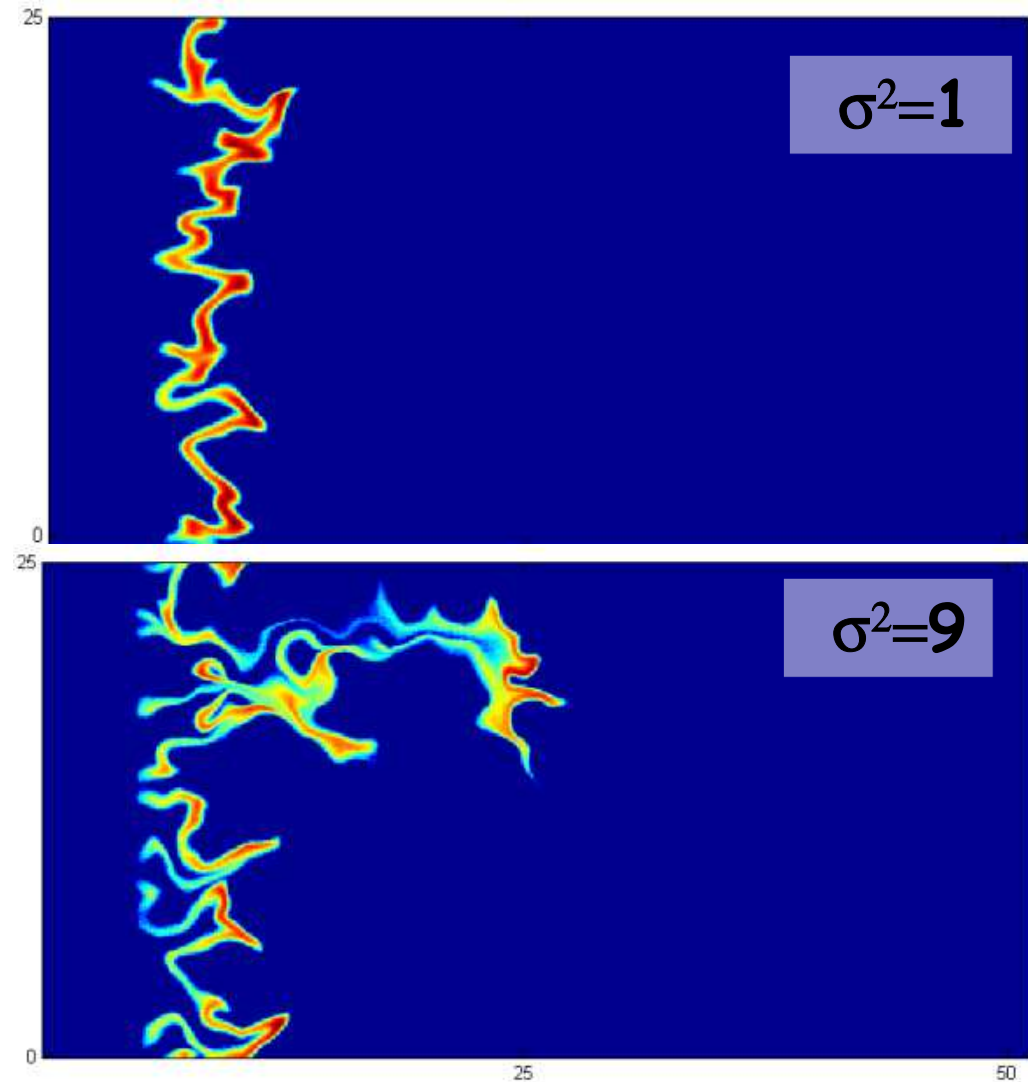
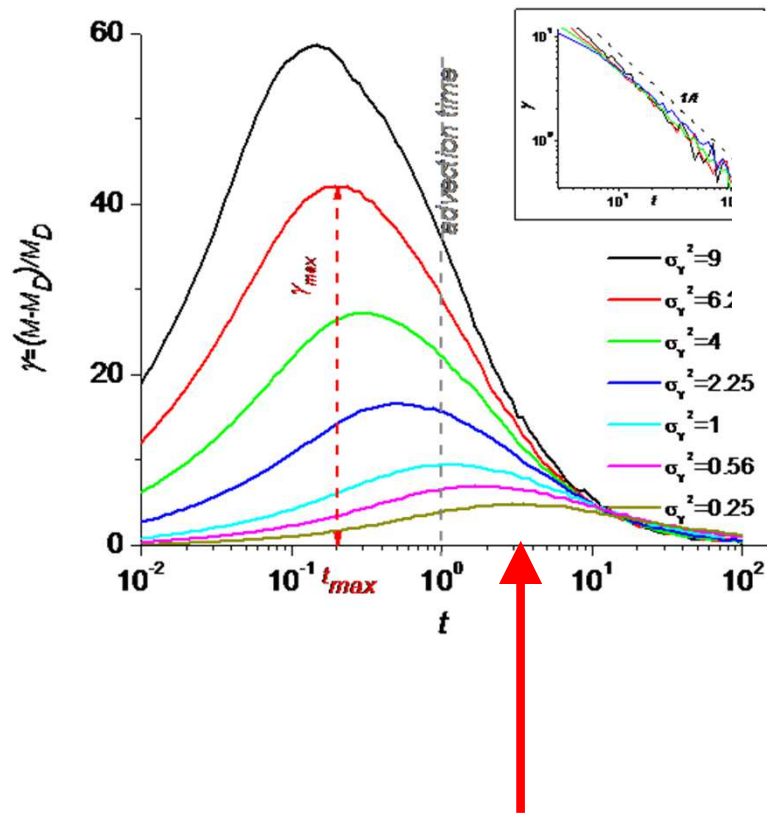
$t=1$





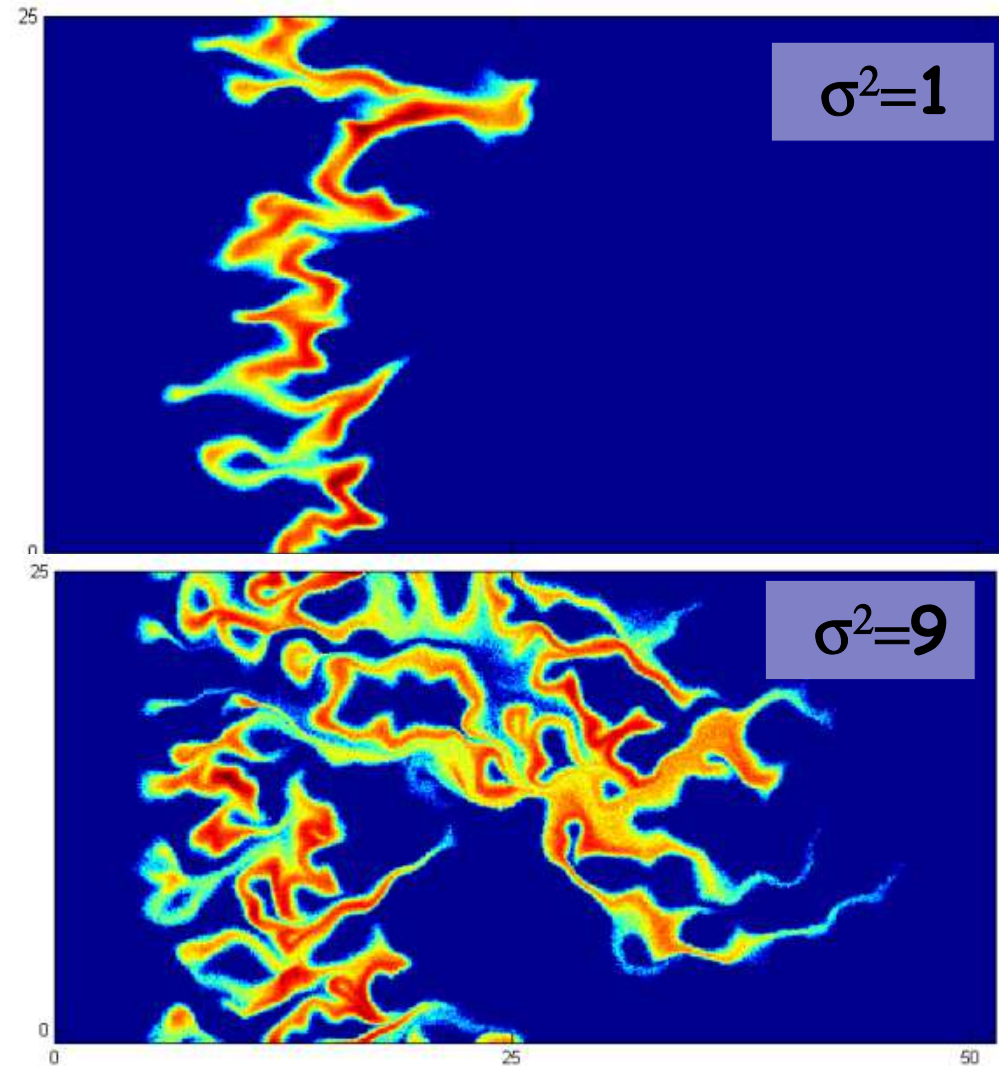
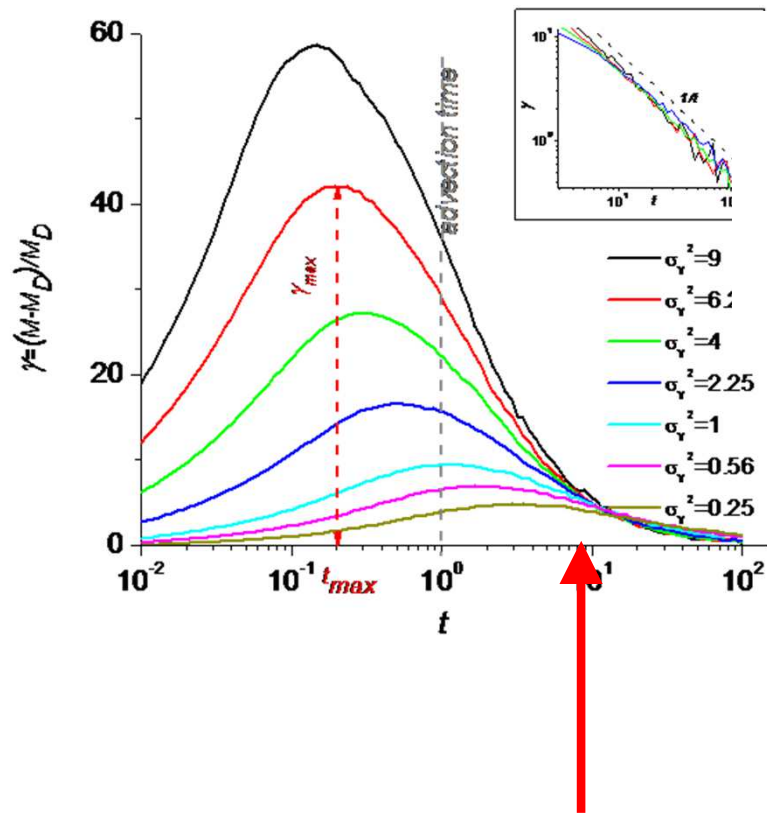
# understanding the $\gamma$ function

$t=3.3$



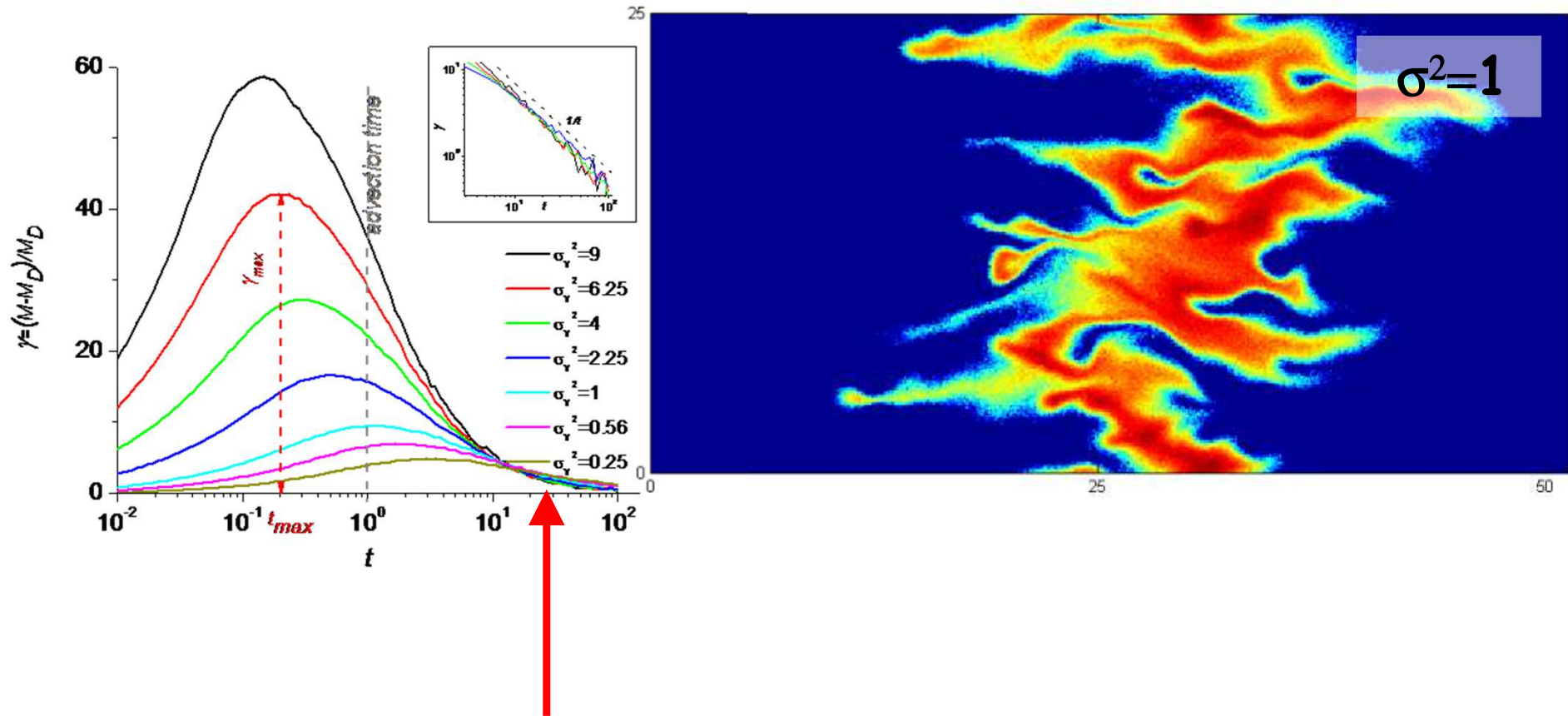
# understanding the $\gamma$ function

$t=9.3$



# understanding the $\gamma$ function

$t=24$



# Variance of $c'$

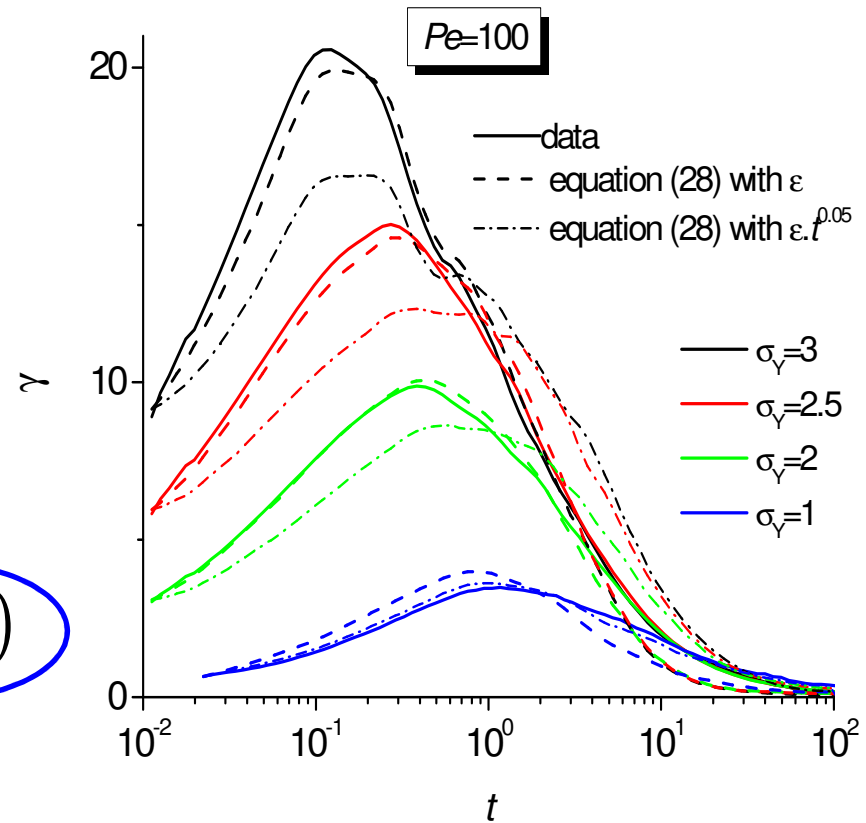
[Kapoor and Gelhar, 1994;  
Kapoor and Kitanidis, 1998]

Smoothing (variance  
reduction by diffusion)

$$M_2'(t) + \frac{2d}{(a \varepsilon(t))^2} M_2(t) = -M_G'(t)$$

Mixing scale (Le  
Borgne et al, 2011)

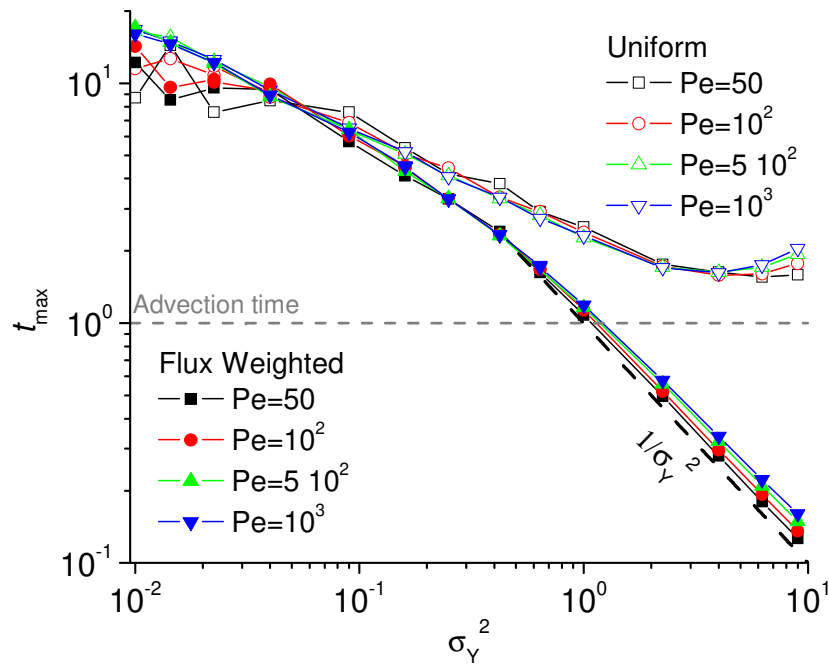
Velocity shear  
creates disorder



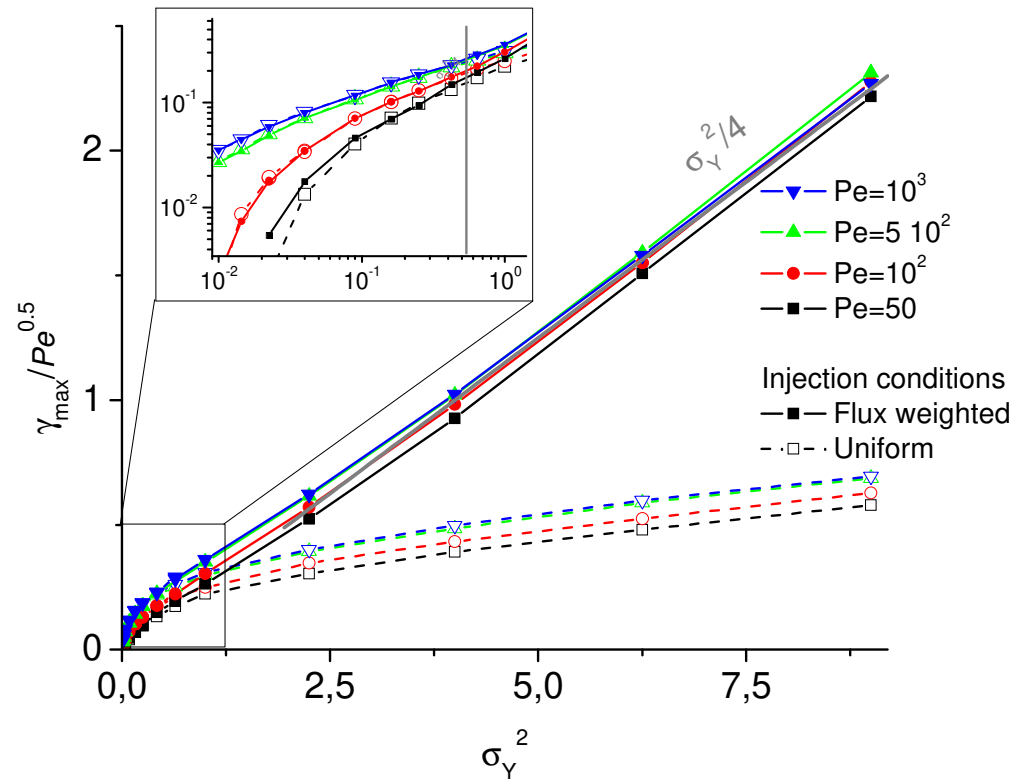
It works!

(De Dreuzy et al., WRR, 2012)

# Characterizing $\gamma_{\max}$ and $t_{\max}$



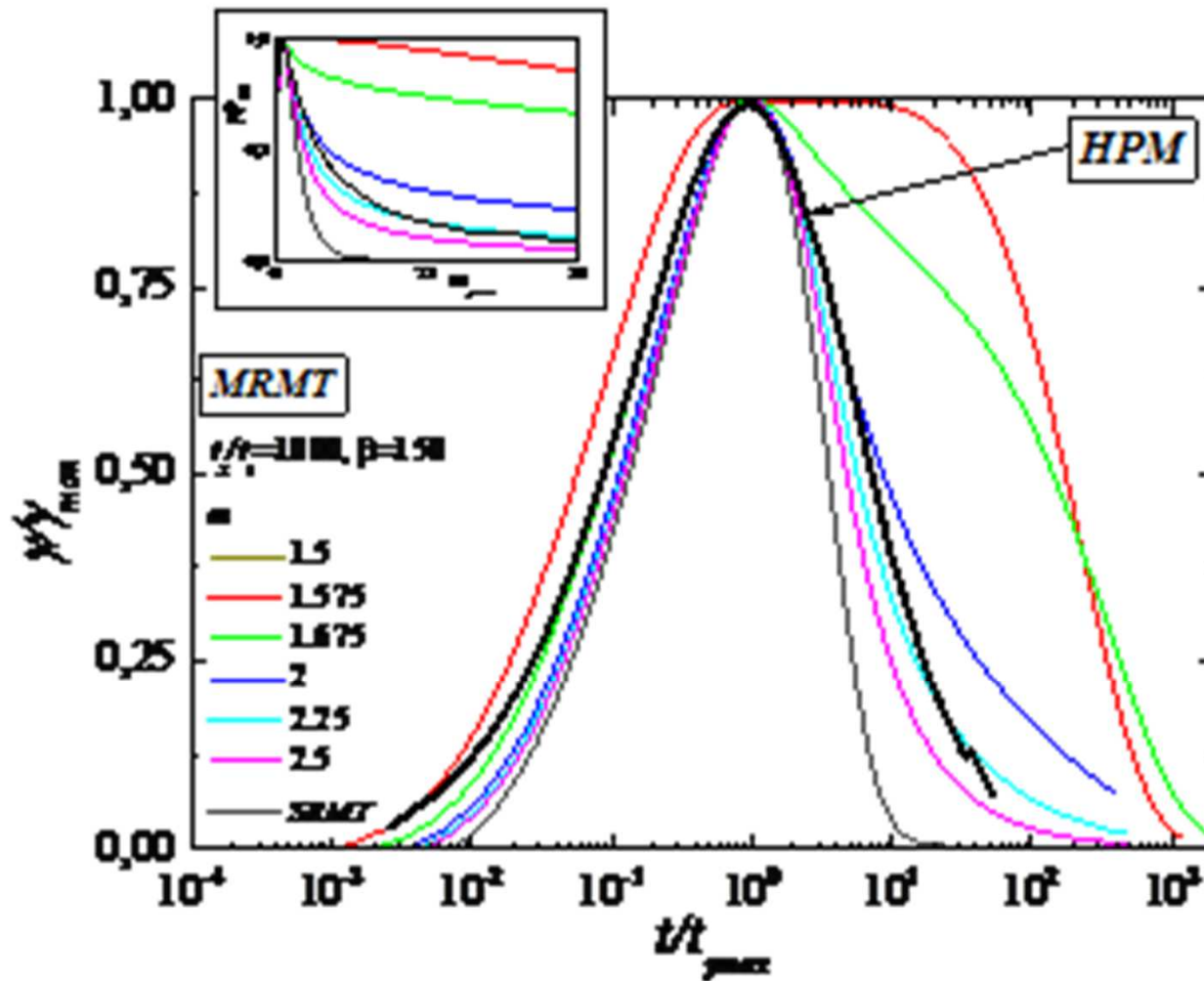
$t_{\max}$  Drops down with  $\gamma$  variance



$\gamma_{\max} / \sqrt{Pe}$  Grows linearly with  $\gamma$  variance

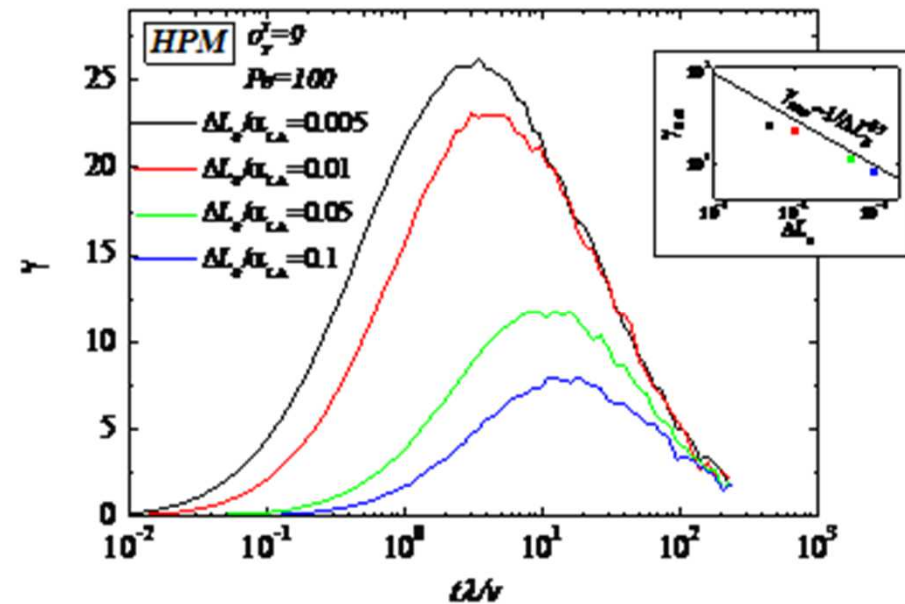
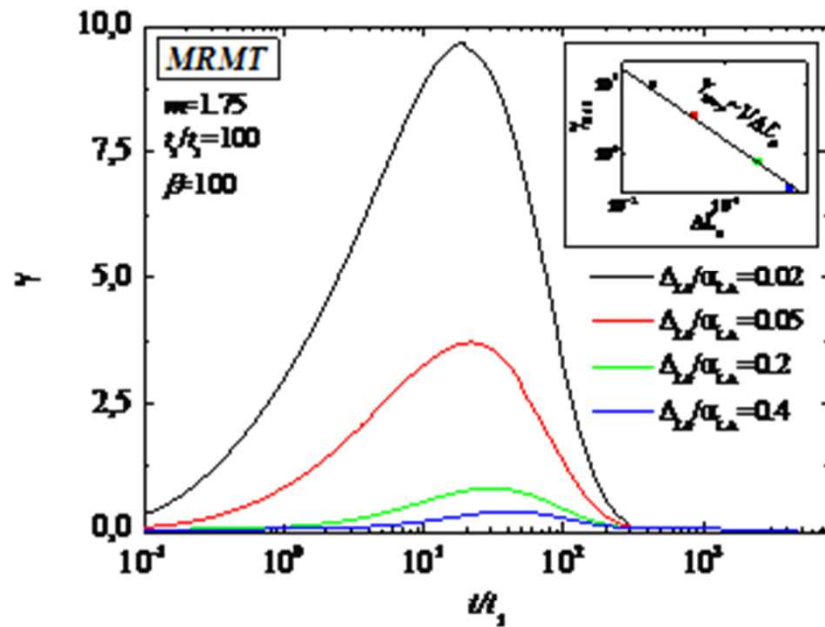
# MRMT formulations do reproduce the shape of gamma

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# But not the actual values!



# Summary and conclusions

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- Spreading can be described by the pdf and transition pdf of veloc, which leads to CTRW, MRMT, fADE,...
  - These formulations overcome the ADE problems, but rely heavily on a proper characterization of mixing.
  - We developed methodology for effective mixing that relies on the evolution of the variance of  $c'$ .
  - Non local equations parameters (memory function) look valid, but not quite.
  - **Any idea?**
-



## REFERENCES

- Andricevic, R. (1998), Effects of local dispersion and sampling volume on the evolution of concentration fluctuations in aquifers, *Water Resources Research*, 34(5), 1115-1129.
- Benson, D. and Meerschaert, M. M.: A simple and efficient random walk solution of multi-rate mobile/immobile mass transport equations, *Adv. Water Resour.* 32(4), 532-539, 2009.
- Berkowitz, B. and Scher, H.: Theory of anomalous chemical transport in random fracture networks, *Phys. Rev. E* 57(5), 5858-5869, 1998.
- Bijeljic, B. and Blunt, M.J., 2006, Pore-scale modeling and continuous time random walk analysis of dispersion in porous media, *Water Resour. Res.* 42, W01202, doi:10.1029/2005WR004578
- Brusseau, M. L., Jessup, R. E., and Rao, P. S. C.: Modeling the transport of solutes influenced by multiprocess nonequilibrium, *Water Resour. Res.* 25(9), 1971-1988, 1989.
- Bolster, D., F. J. Valdés-Parada, T. Le Borgne, M. Dentz, and J. Carrera (2011), Mixing in confined stratified aquifers, *Journal of Contaminant Hydrology*, 120-121, 198-212.
- Carrera, J. (1993). An overview of uncertainties in modelling groundwater solute transport. *J. Cont. Hydrol.*, 13:23-84.
- Carrera, J., Sánchez-Vila, X., Benet, I., Medina, A., Galarza, G., and Guimerà, J.: On matrix diffusion: formulations, solution methods and qualitative effects, *Hydrogeol. J.* 6, 178-190, 1998.
- de Simoni, M., J. Carrera, X. Sanchez-Vila, and A. Guadagnini (2005), A procedure for the solution of multicomponent reactive transport problems, *Water Resources Research*, 41(11). DOI: W11410, Artn w11410.
- Dentz, M. and Berkowitz, B.: Transport behavior of a passive solute in continuous time random walks and multirate mass transfer, *Water Resour. Res.* 39(5), 1111, doi:10.1029/2001WR001163, 2003.
- Grassberger, P., and I. Procaccia (1983), Characterization of strange attractors, *Physical Review Letters*, 50(5), 346-349. DOI: 10.1103/PhysRevLett.50.346.
- Gouze, P., Melean, Y., Le Borgne, T., Dentz, M., and Carrera, J.: Non-Fickian dispersion in porous media explained by heterogeneous microscale matrix diffusion, *Water Resour. Res.* 44, W11416, doi:10.1029/2007WR006690, 2008.
- Haggerty, R. and Gorelick, S. M.: Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity, *Water Resour. Res.* 31(10), 2383-2400, 1995.
- Haggerty, R., McKenna, S. A., and Meigs, L. C.: On the late-time behavior of tracer test breakthrough curves, *Water Resour. Res.* 36(12), 3467-3479, 2000.
- Kapoor, V., and P. K. Kitanidis (1998), Concentration fluctuations and dilution in aquifers, *Water Resources Research*, 34(5), 1181-1193.

## REFERENCES (2)

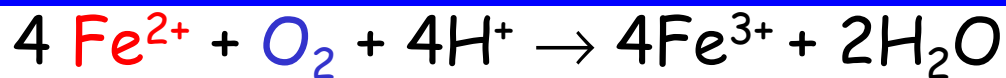
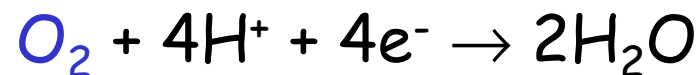
- Kitanidis, P. K. (1994), The concept of the dilution index, *Water Resources Research*, 30(7).
- Le Borgne, T., M. Dentz, D. Bolster, J. Carrera, J.-R. de Dreuzy, and P. Davy (2010), Non-Fickian mixing: Temporal evolution of the scalar dissipation rate in heterogeneous porous media, *Advances in Water Resources*, 3(12), 1468-1475.
- Le Borgne, T., M. Dentz, and J. Carrera, A Lagrangian statistical model for transport in highly heterogeneous velocity fields. *Phys. Rev. Lett.*, 101, 090601, 2008.
- Pope, S. (2000), *Turbulent flows*, Cambridge University Press.
- Ray, Ch., Ellsworth, T. R., Valocchi, A. J. and Boast, Ch. W.: An improved dual porosity model for chemical transport in macroporous soils, *J. Hydrol.* 193(1-4), 270-292, 1997.
- Salamon, P., Fernández-García, D., and Gómez-Hernández, J. J.: Modeling mass transfer processes using random walk particle tracking, *Water Resour. Res.* 42, W11417, doi:10.1029/2006WR004927, 2006.
- Tennekes, H. L., J. L. (1972), *A first course in turbulence*, MIT press, Cambridge, Mass.
- Tonina, D., and A. Bellin (2008), Effects of pore-scale dispersion, degree of heterogeneity, sampling size, and source volume on the concentration moments of conservative solutes in heterogeneous formations, *Advances in Water Resources*, 31(2), 339-354. DOI: 10.1016/j.advwatres.2007.08.009.
- White, A. F. and Brantley, S. L. (2003). The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and in the field? *Chem. Geol.*, 3-4:479-506.
- Villermaux, J., and J. C. Devillon (1972), Représentation de la coalescence et de la redispersion des domaines de ségrégation dans un fluide par un modèle d'interaction phénoménologique, paper presented at Proc. of 2nd International Symposium Chem. React. Engng., Elsevier
- Willmann, M., Carrera, J., and Sánchez-Vila, X.: Transport upscaling in heterogeneous aquifers: what physical parameters control memory functions?, *Water Resour. Res.* 44, W12437, doi:10.1029/2007WR006531, 2008.
- Willmann, M., Carrera, J., Sánchez-Vila, X., and Silva, O.: Coupling of mass transfer and reactive transport for non-linear reactions in heterogeneous media, *Water Resour. Res.*, submitted, 2009.

# Redox reactions

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Redox reactions involve exchange of electrons ( $e^-$ )

The species giving electrons away is called "electron donor", the one receiving is the "electron acceptor", eg.



Iron is donor (is oxidized). Oxygen is acceptor (is reduced)

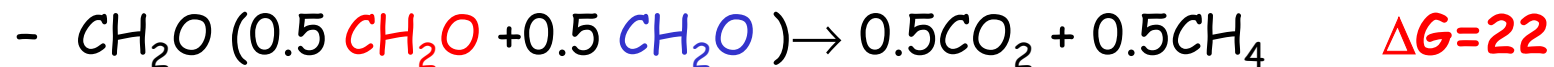
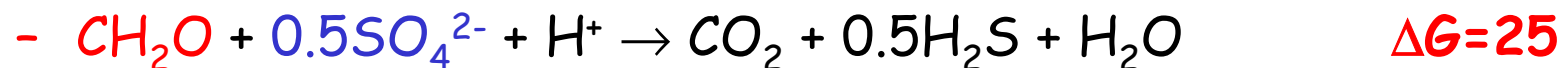
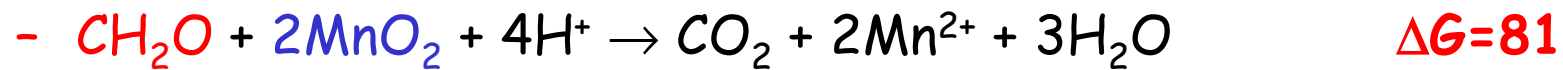
These reactions are exothermic. Life on Earth is sustained on the energy freed by these reactions.





# Biochemical reactions: the natural redox cycle

- Redox reactions catalyzed by microorganisms
- Special case: organic matter **degradation**, the electron donor is organic matter (generically,  $\text{CH}_2\text{O}$ ). The **natural sequence** is:



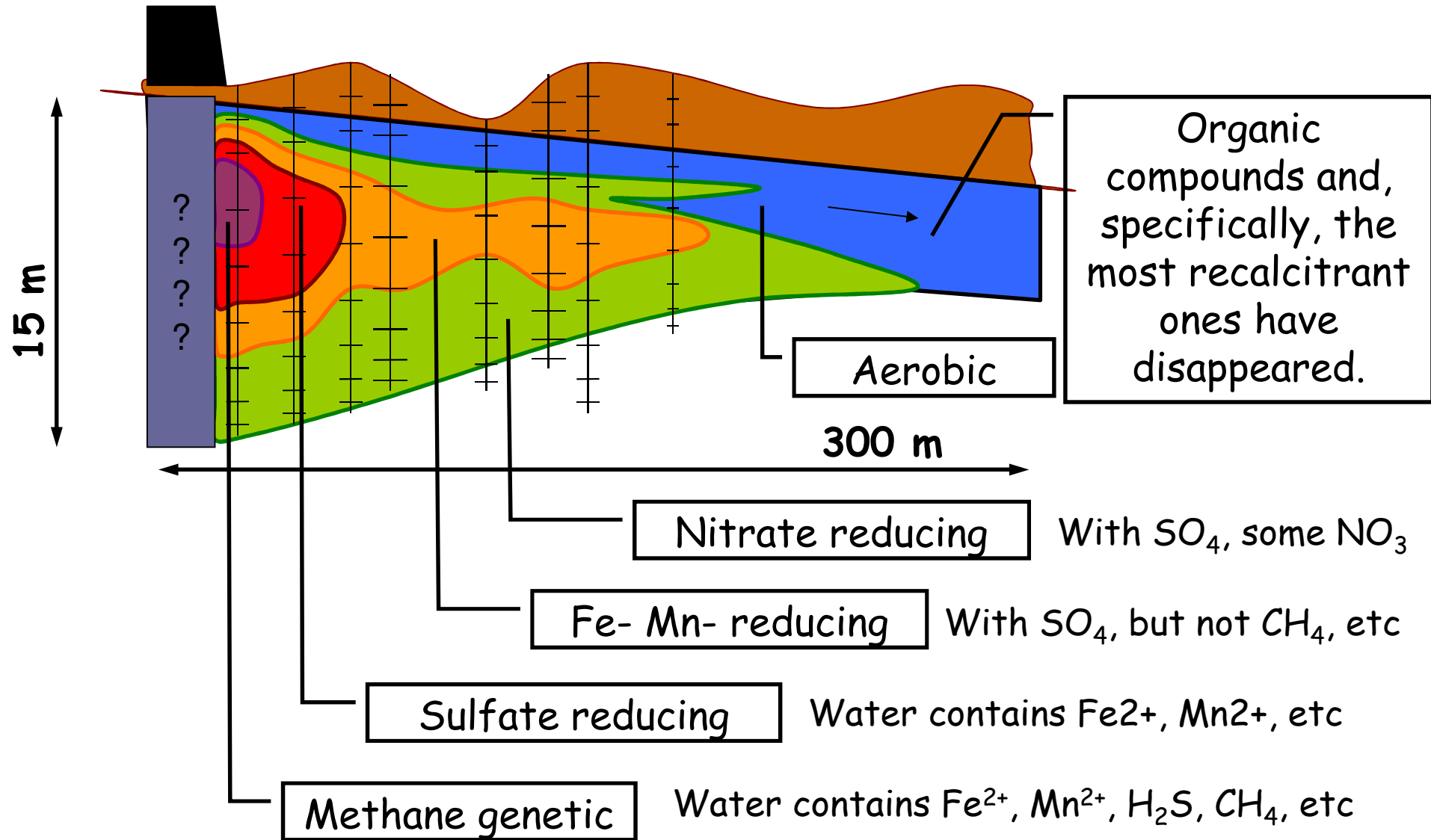
The most **efficient organisms dominate each stage**, inhibiting the development of the ones below. Yet, their success is their nemesis, as they **exhaust their electron acceptor**. This opens the path for the **next organism down the ladder**, which dominates the next stage. Overall, this leads to a **natural zonation**.

# Why biological degradation

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- Control metal mobility
  - Many immobile when sulphide present
  - Some immobile in aerobic conditions
- Control degradation of organic matter
- Highly reducing conditions allow eliminating "recalcitrant" compounds
  - That are not eliminated in "normal" treatment
  - That are often endocrine inhibitors

# Redox zones at the Vejen (Denmark) landfill



# Conclusions

---

- Is Reactive transport needed?
    - Reaction (rate , where, when, under which conditions) are controlled by transport.
  - Can be understood?
    - All it takes is to understand components
    - The difficult part is to choose the relevant species and reactions.
  - Can be solved efficiently?
    - Similar effort as conservative transport
-



# But

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Reactions are driven by **disequilibrium**

Disequilibrium is driven by **actual mixing**

We need to know how to evaluate actual mixing!

Current stochastic transport theories fail to do so!

