REACTIVE TRANSPORT MODELING: AN INTRODUCTION

Jesus Carrera

GHS, IDAEA
CSIC (Spanish Research Council)
Barcelona, Spain

Contents

- The two basic ingredients
- Example: role of mixing
- Transport with eq. Reactions
- Generalization
- Mixing and spreading
- Applications

Ingredient 1: solute transport

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

Ingredient 2: Chemical reactions: Stoichiometric matrix

- Assume a chemical system

$$CO_3^{2-} = HCO_3^- - H^+$$
$$CO_2 = HCO_3^- + H^+ - H_2O$$
$$Ca^{2+} = CaCO_{3s} + H^+ - HCO_3^-$$

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)

$$\mathbf{S} = \left(\begin{array}{cc|ccc|cc} H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Ca^{2+} & CaCO_{3s} & H_2O \\ -1 & 1 & -1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & -1 & 0 & 0 & -1 \\ 1 & -1 & 0 & 0 & -1 & 1 & 0 \end{array}\right)$$

Primary Secondary Constant Ac.

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

- Reaction rate: Mass balance

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

Reactive transport

- Reactions

$r_1 \quad CO_3^{2-} = HCO_3^- - H^+$

$r_2 \quad CO_2 = HCO_3^- + H^+ - H_2O$

$r_3 \quad Ca^{2+} = CaCO_{3s} + H^+ - HCO_3^-$

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

- Transport of all species

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

$$\phi \frac{\partial CO_3^{2-}}{\partial t} = L(CO_3^{2-}) - r_1 \qquad \phi \frac{\partial CO_2}{\partial t} = L(CO_2) - r_2 \qquad \phi \frac{\partial Ca^{2+}}{\partial t} = L(Ca^{2+}) - r_3$$

- Recall **S**

$$\mathbf{S} = \left(\begin{array}{cc|ccc|cc} H^+ & HCO_3^- & CO_3^{2-} & CO_2 & Ca^{2+} & CaCO_{3s} & H_2O \\ -1 & 1 & -1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & -1 & 0 & 0 & -1 \\ 1 & -1 & 0 & 0 & -1 & 1 & 0 \end{array}\right)$$

Primary | Secondary | Constant Ac.

Formulation of Reactive transport problems

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

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

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

Seek tricks and/or simplifications

So… objectives of this presentation

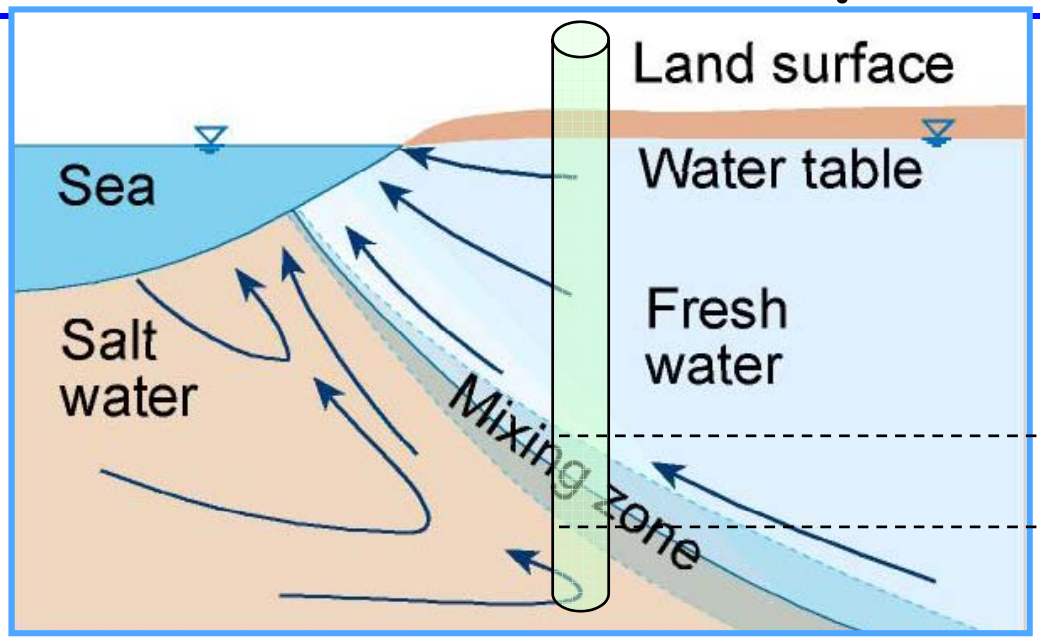
- Is reactive transport needed?
- Can be understood?
- Can be solved efficiently?

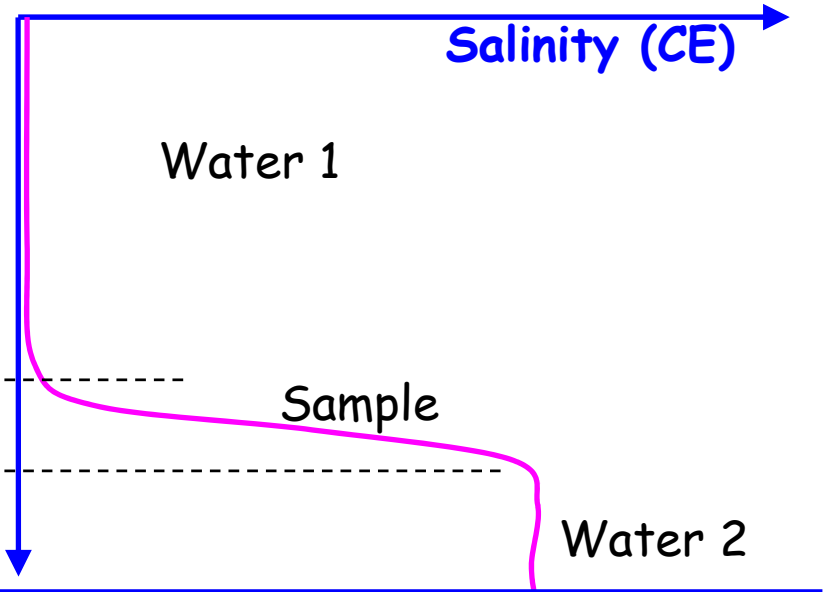
… and the answer is YES

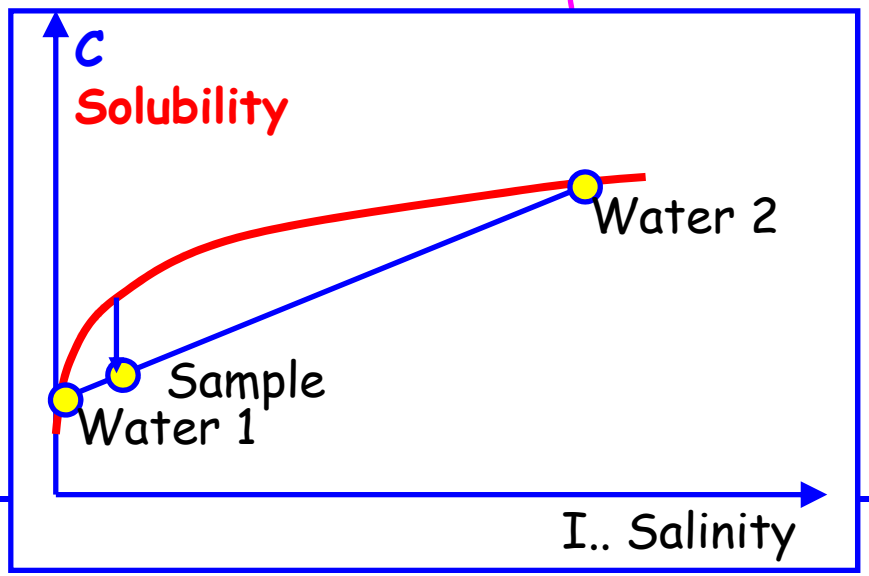
- Do we **really** know how to do it?

… not quite… but getting there

Why worry reactive transport?
Ex: Karst development in coastal areas



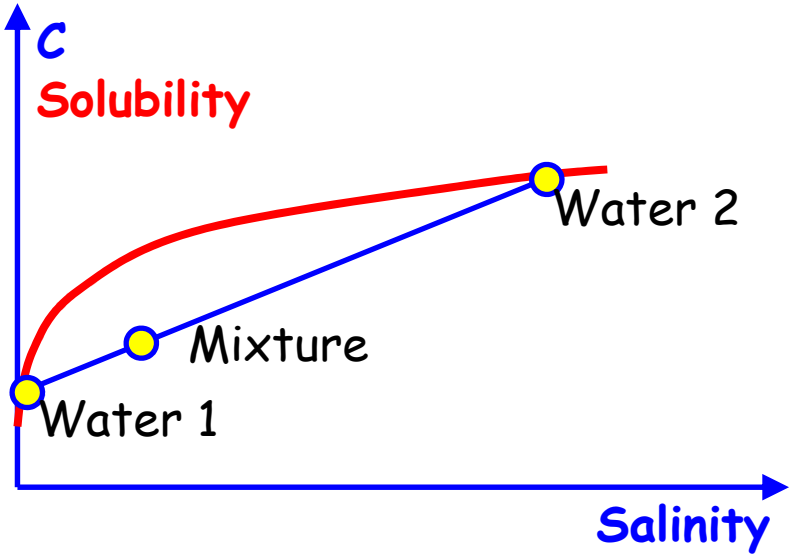




Aparently, the sample is undersaturated. Yet, waters 1 and 2 are in equilibrium.

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

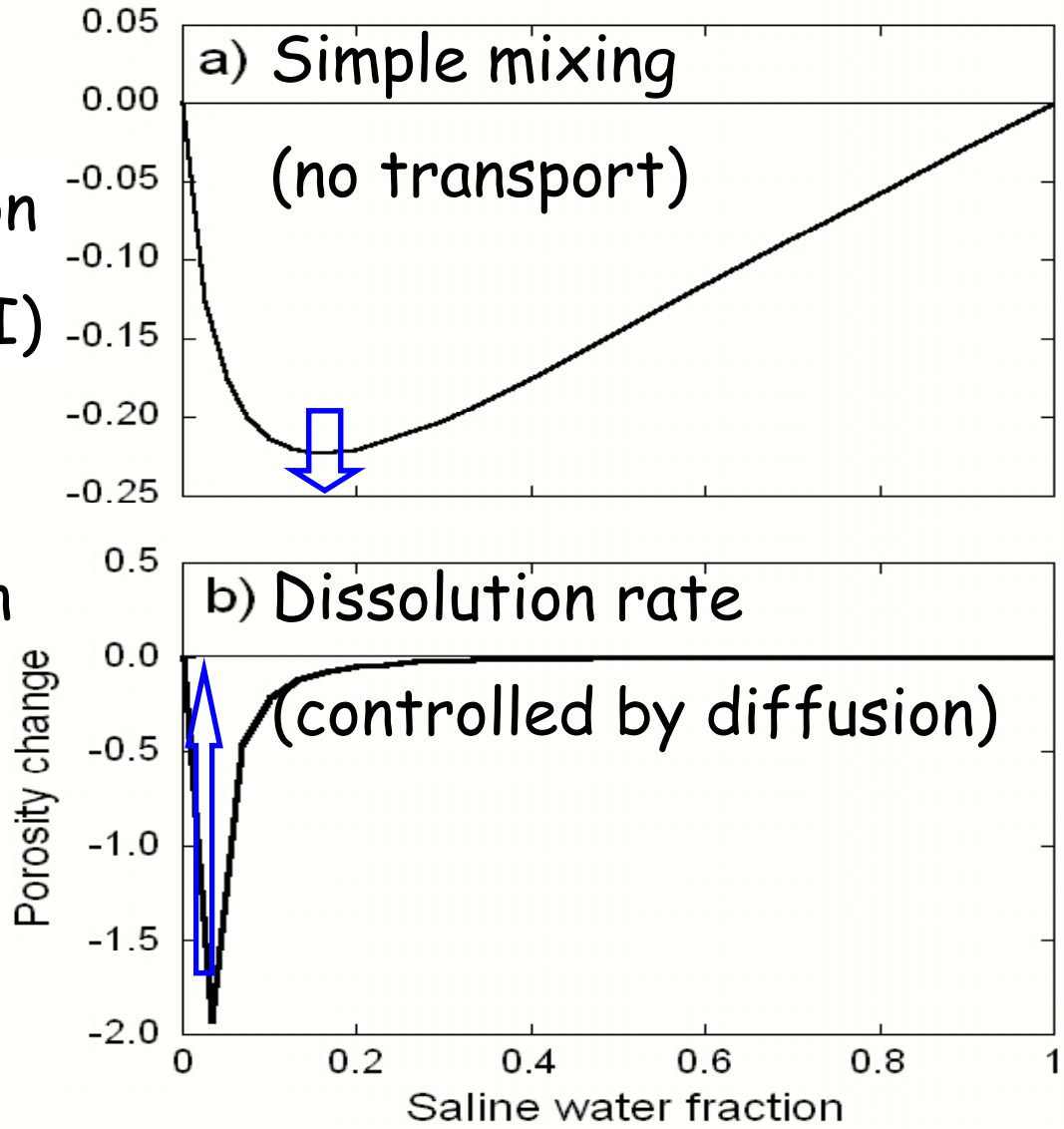
freshwater **calcite** **saltwater**

(Rezaei et al, 2005)

SI & r

Saturation Index (SI)

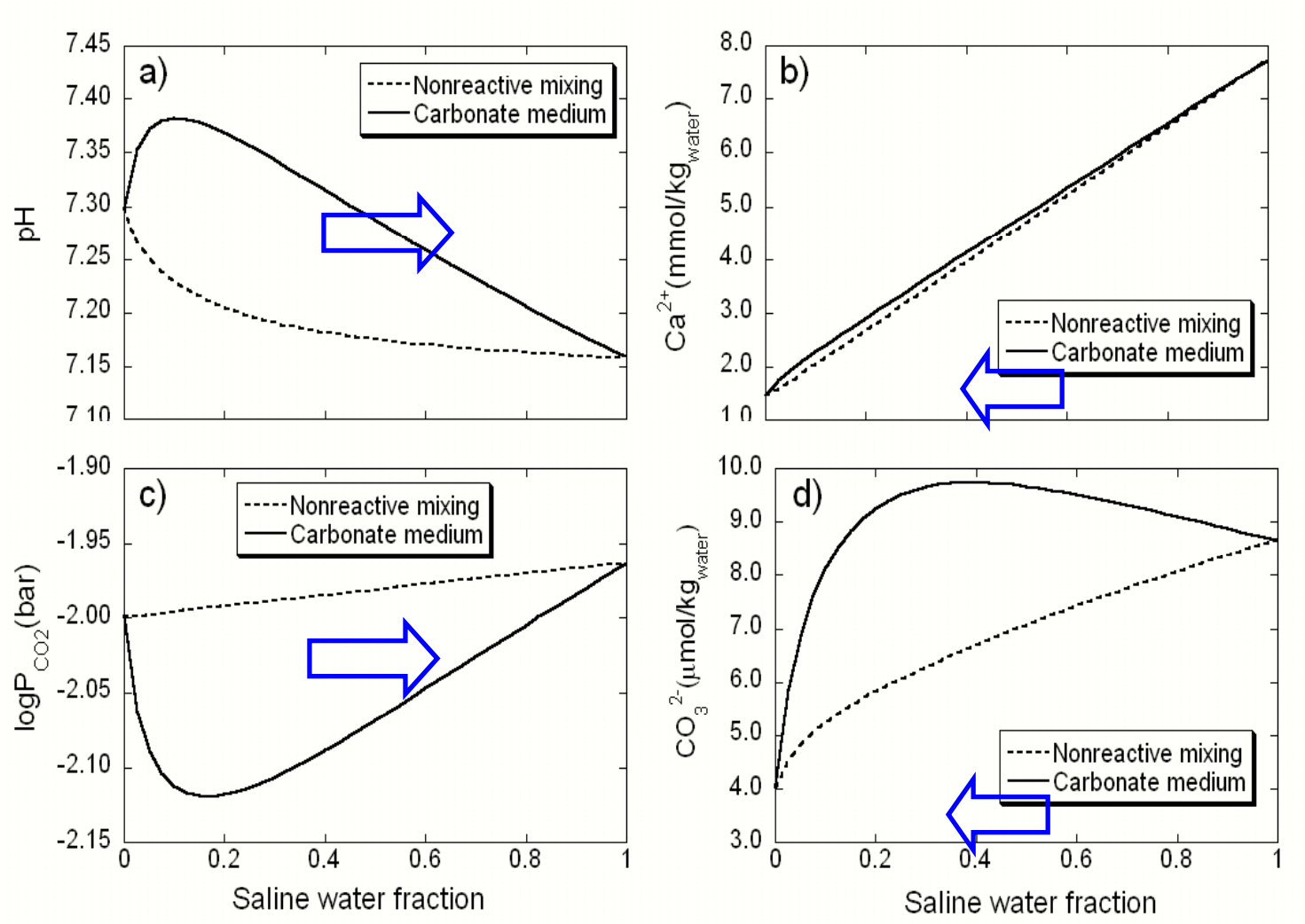
Reaction Rate



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

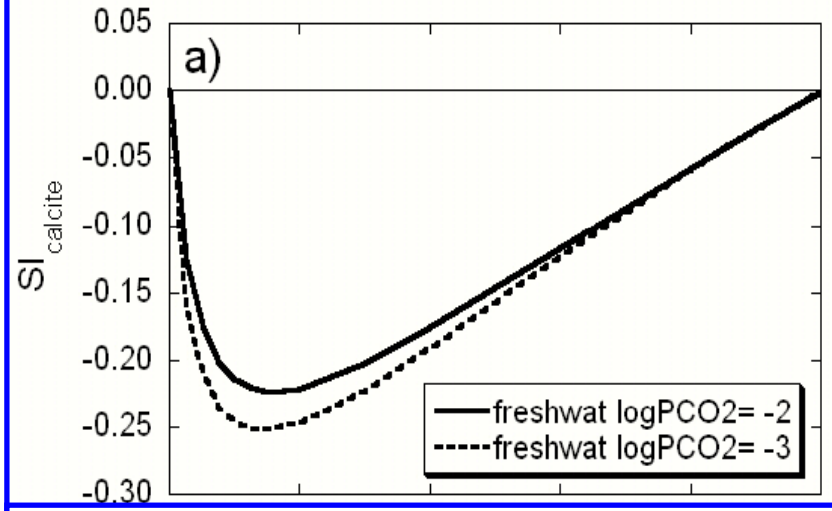
Dissolution rate proportional to Diff coeff. and maximum at the fresh water end

Speciation

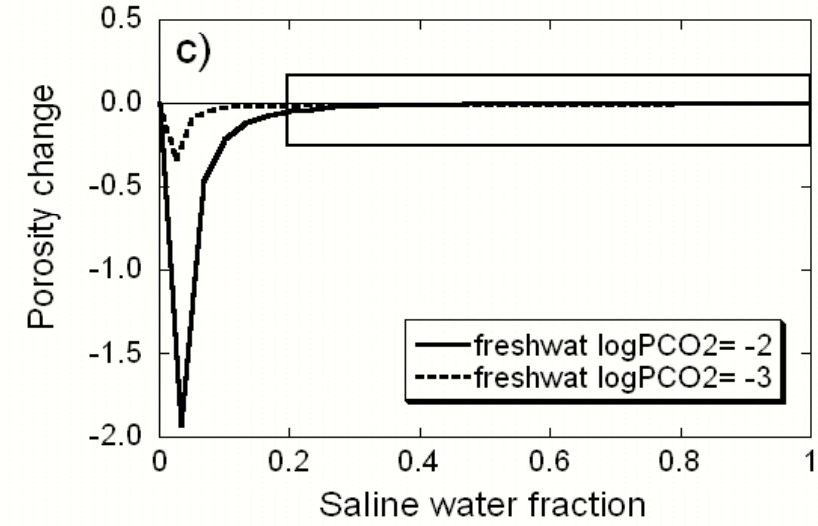


Dissolution causes diffusion of CO_2 (acidity) at the freshwater end, which drives further dissolution

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

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?

- 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

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

Choose component matrix U, such that

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

Then,

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

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 U allows these equations to be decoupled!)

Example

- **Chemical system**

$$CO_3^{2-} = HCO_3^- - H^+$$
$$CO_2 = HCO_3^- + H^+ - H_2O$$
$$Ca^{2+} = CaCO_{3s} + H^+ - HCO_3^-$$

- **Stoichiometric Matrix**

$S_e=(S_1 ; -I)$

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

- **Components matrix**

$S_e=(I ; S_1^{\dagger})$

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

- **Components**

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

$$u_2 = HCO_3^- + CO_3^{2-} + CO_2 - Ca^{2+}$$ (Total Inorganic Carbon)

Role of components

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

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

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

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

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

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

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

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

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

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

Reaction $Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_{4s} \Rightarrow \left[Ca^{2+}\right]\cdot\left[SO_4^{2-}\right] = K$

Stoichiometric matrix $\mathbf{S}_e = \begin{pmatrix} -1 & -1 & 1 \end{pmatrix}$

Components: $\mathbf{U} = \begin{pmatrix} 1 & -1 \end{pmatrix} \Rightarrow u = \left[Ca^{2+}\right] - \left[SO_4^{2-}\right]$ is conservative!

Step 2: Solve transport of u

Transport equations

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

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

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

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

Analytical solution for 2 species

Step 3: Speciation

Solve $u = C_1 - C_2$

Together with $C_1 \cdot C_2 = K$

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

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

Step 4: Compute r

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

We obtain $r = \dfrac{\partial^2 C_2}{\partial u^2}\left[\nabla u^T \cdot \mathbf{D} \cdot \nabla u\right]$

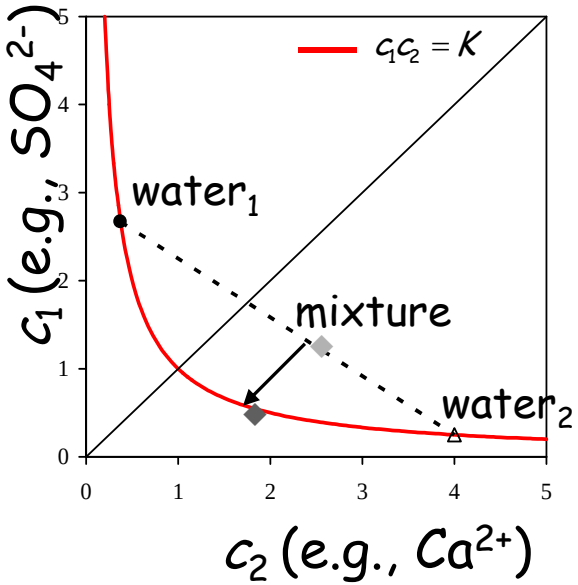
Transport

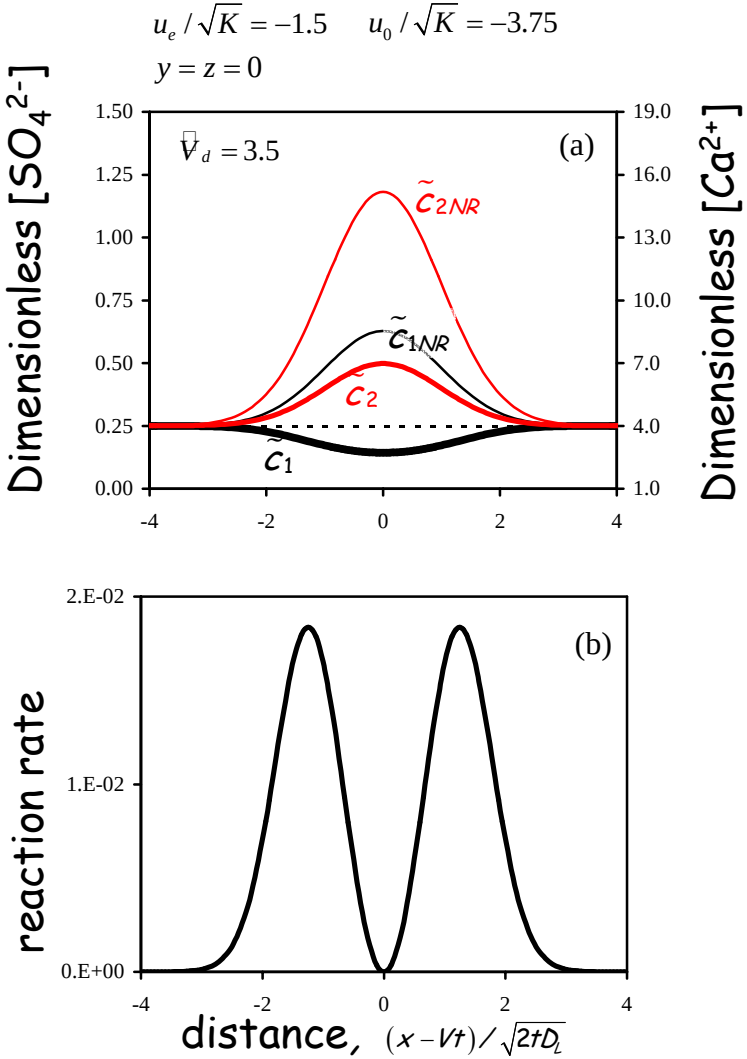
Chemistry

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

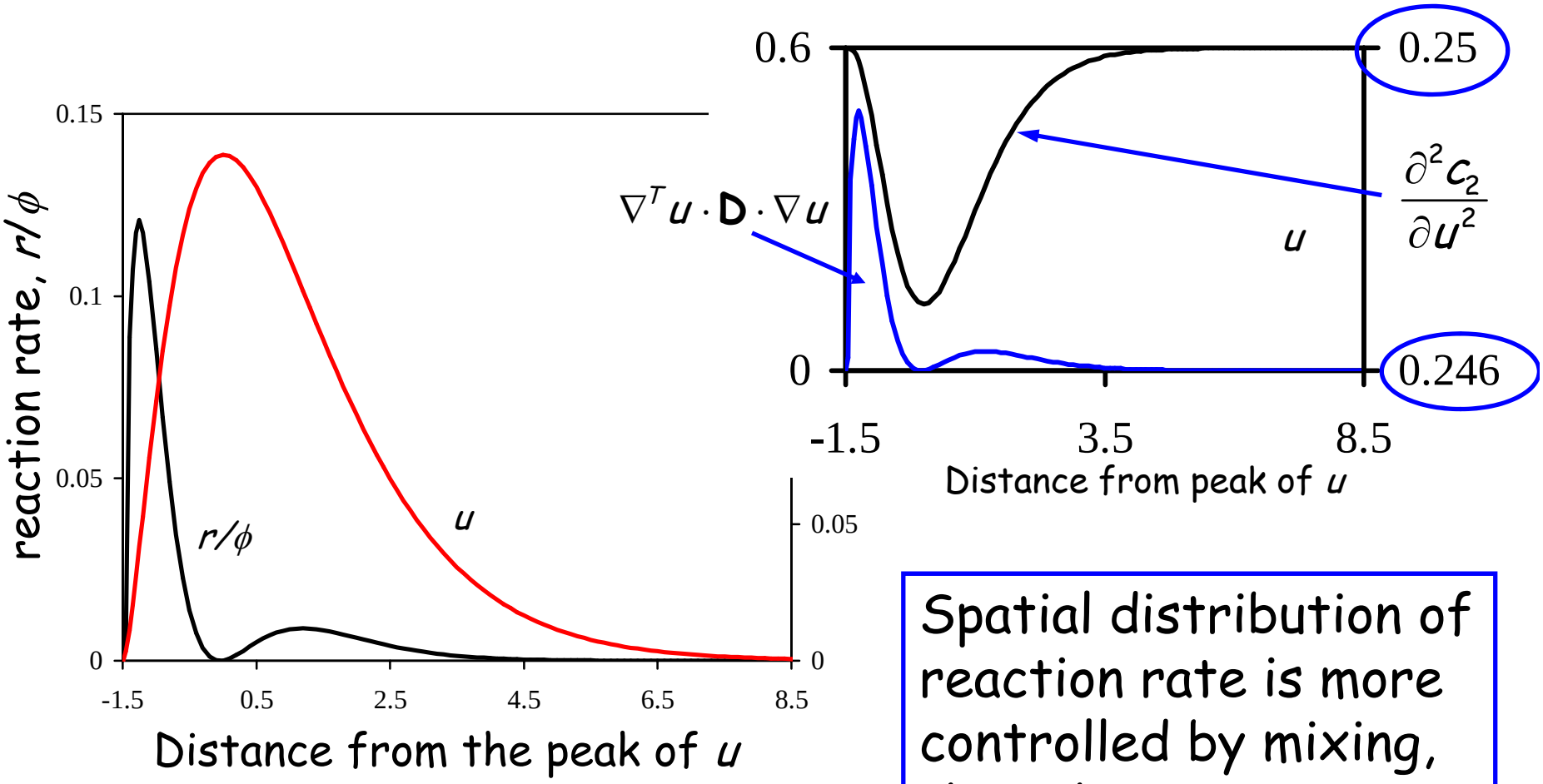
Solution of binary system for pulse input

$$u(x,t) = u_0 + \frac{18}{(2\pi)^{1/2}} \frac{u_e}{V_d} exp\left[-\frac{1}{2}\left(\frac{(x-Vt)^2}{2tD_L} + \frac{y^2+z^2}{2tD_T} \right) \right]$$





Spatial distribution of reaction rate

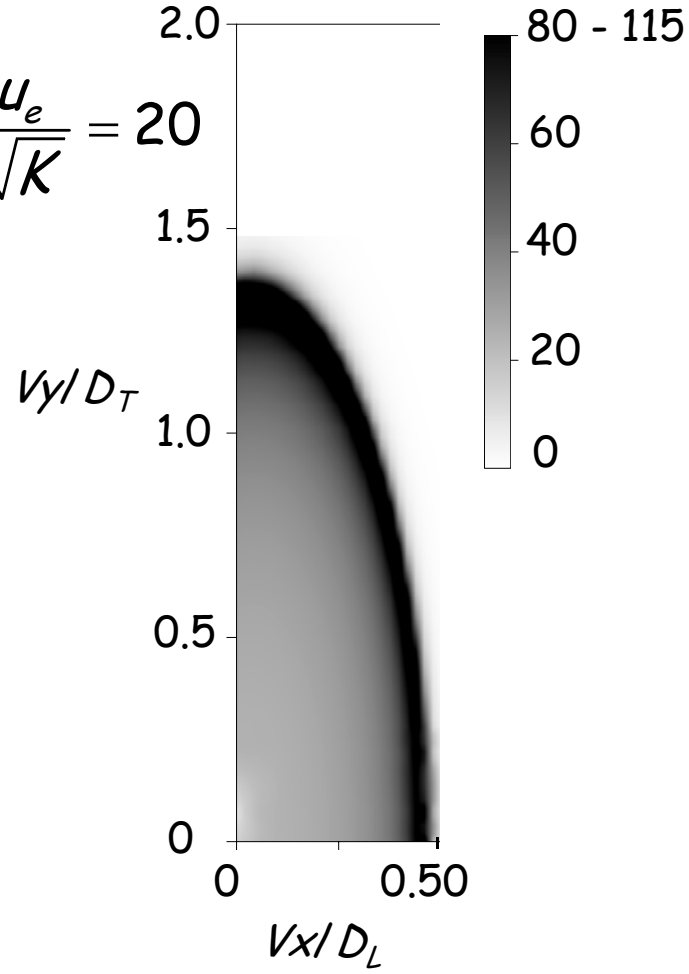


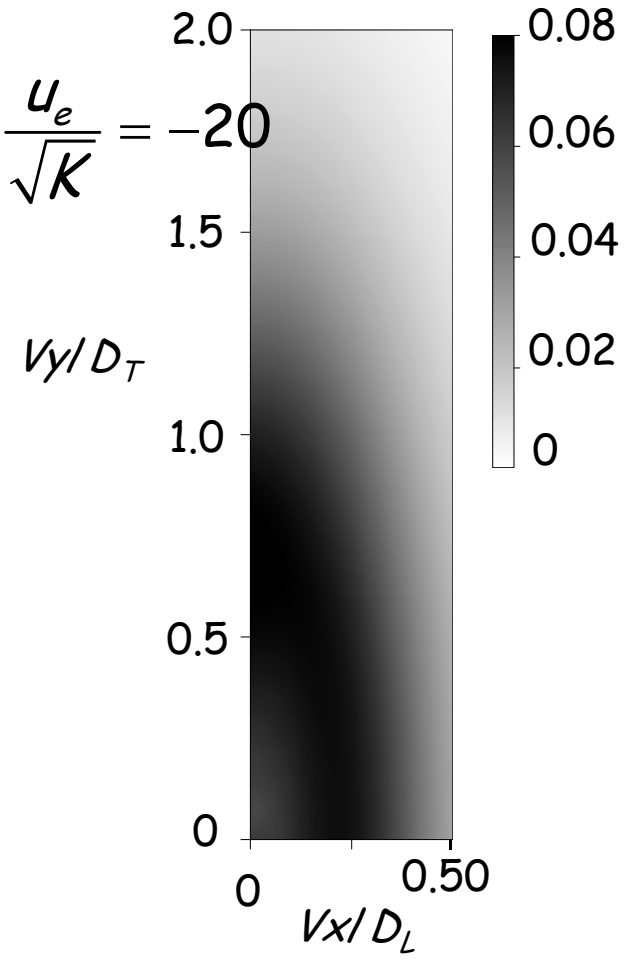
Spatial distribution of reaction rate is more controlled by mixing, than chemistry

Spatial distribution of total precipitate

$$\tilde{r}_t = \frac{\int_0^{\infty} r dt}{\sqrt{K}}$$

$$\frac{u_0}{\sqrt{K}} = -20$$





2nd Conclusion

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, one will suffice by working with mixing ratios… (Desimoni et al., 2007)
3. **Mixing drives fast reactions**

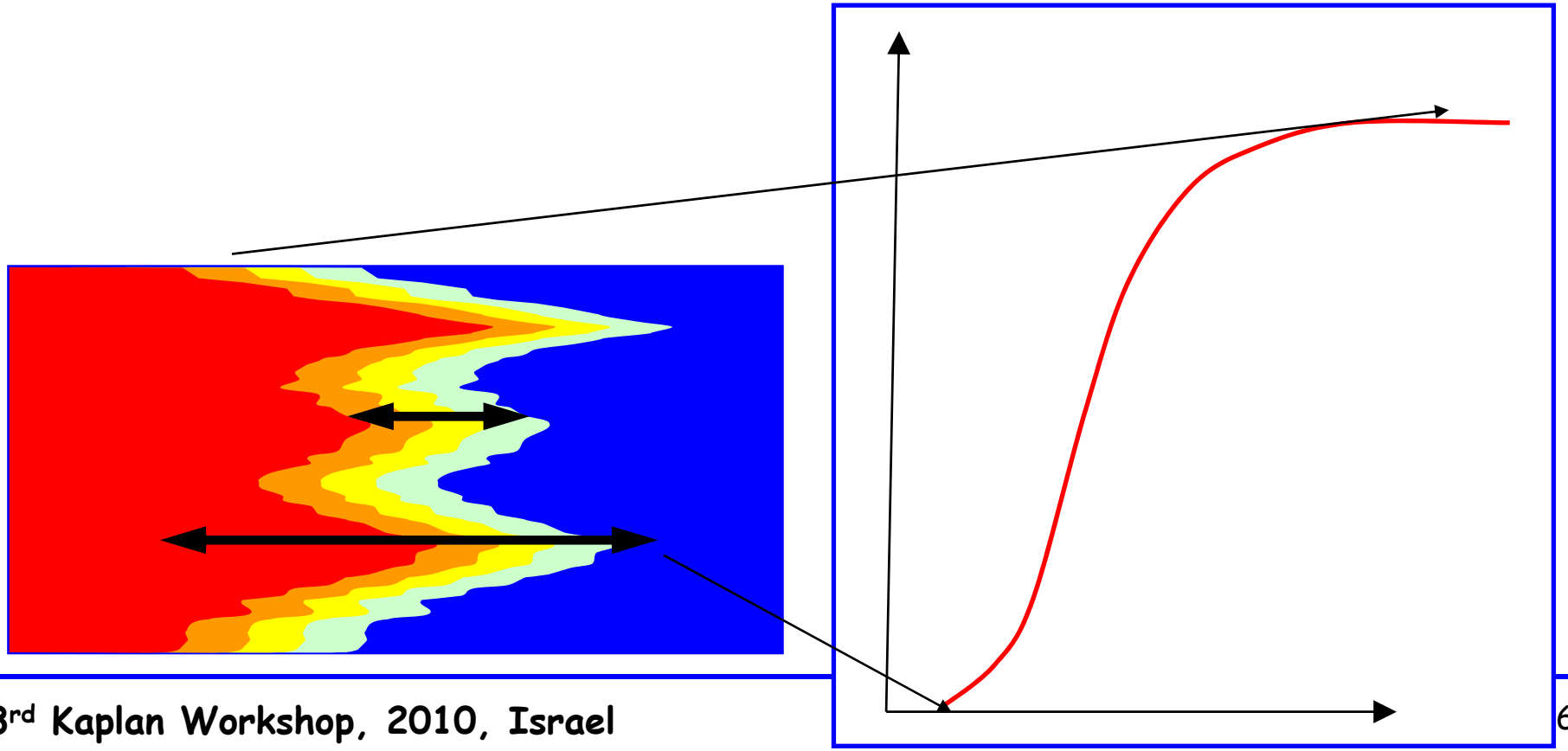
But do we know how to simulate mixing?

- Traditionally, mixing is simulated by means of dispersion.

Dispersion

Traditionally defined from integrated breakthrough curves, measures spreading

Mixing controls reactions

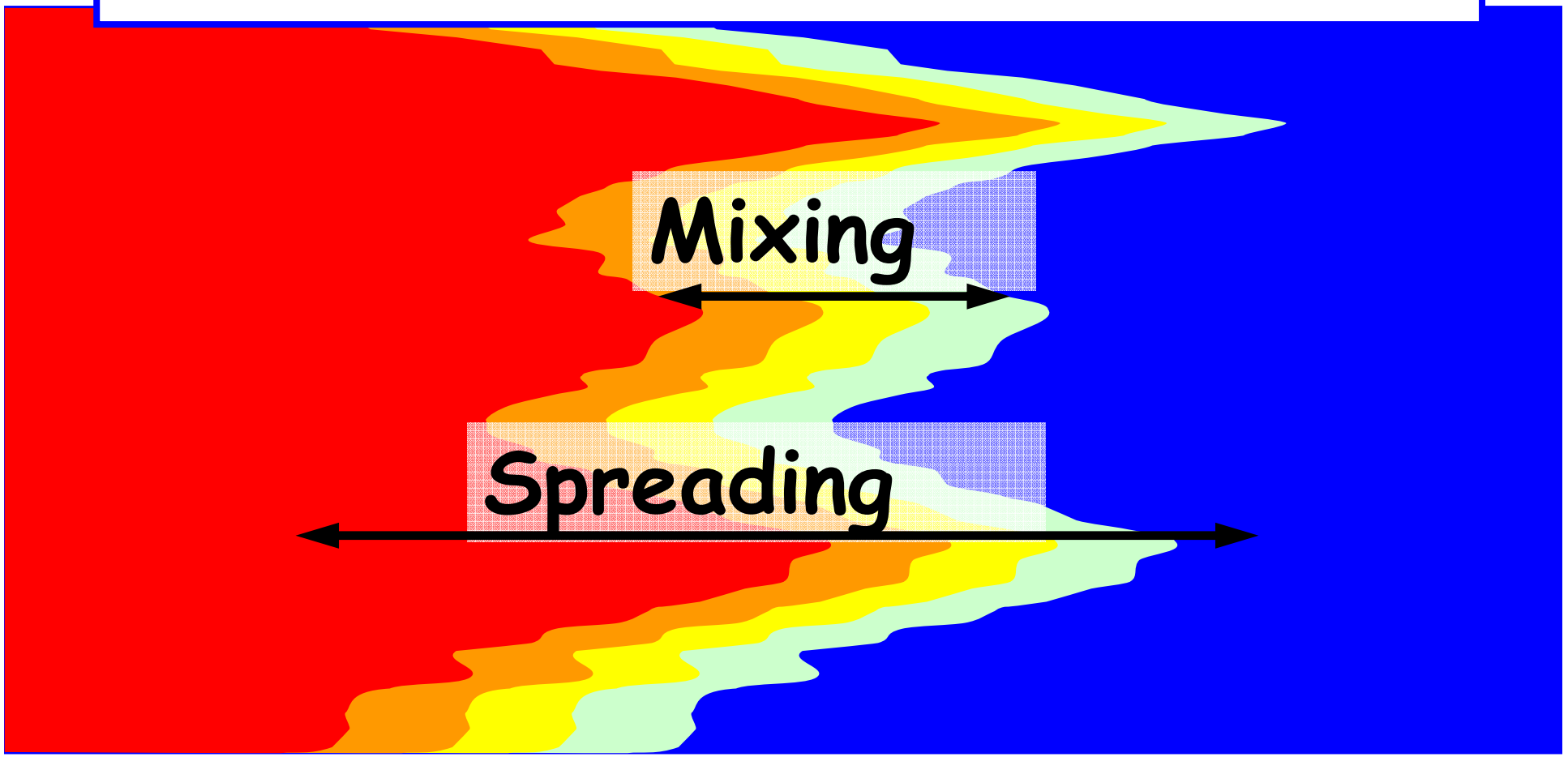


Spreading and Mixing

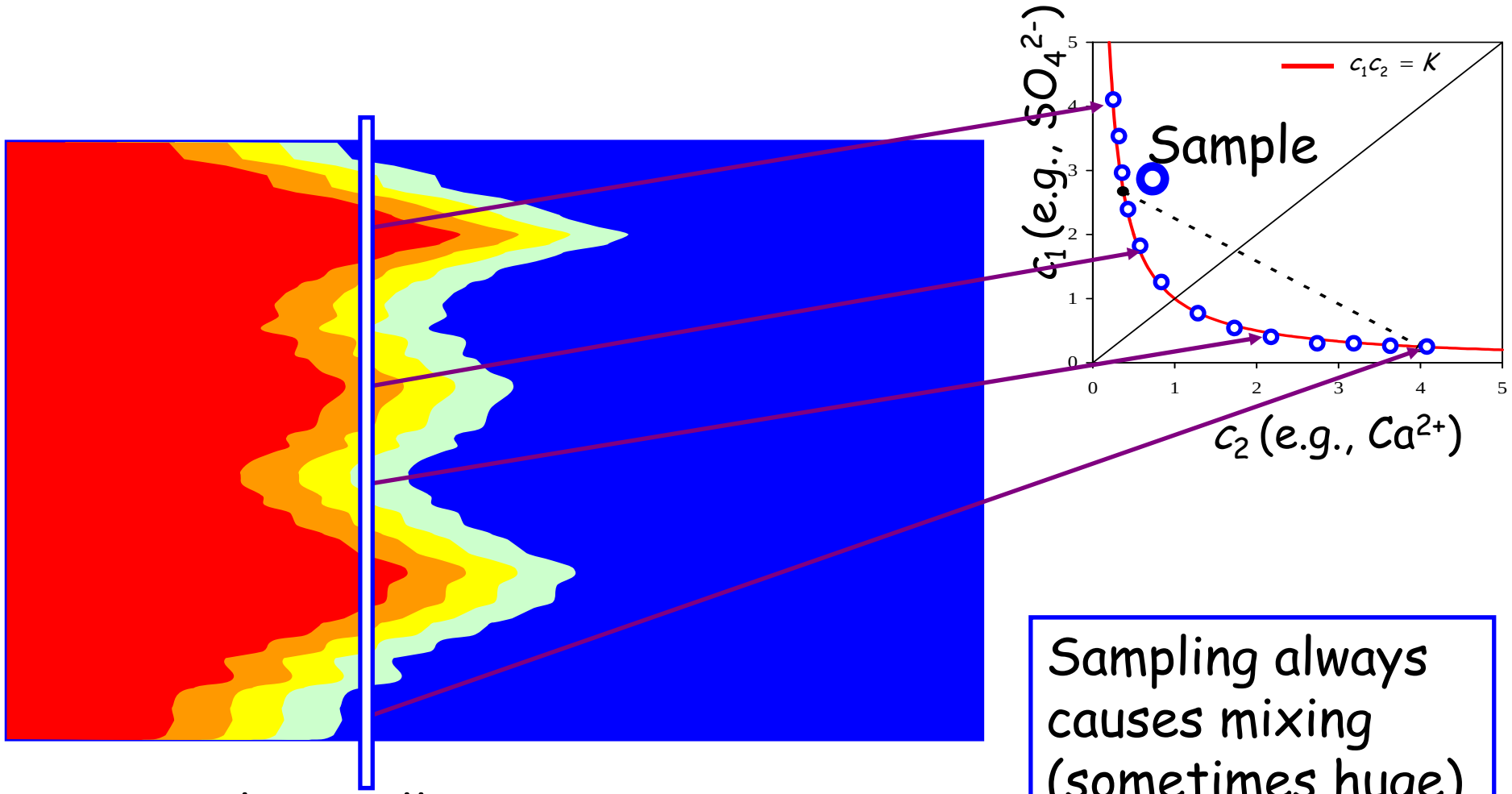
Spreading ➔ extension ➔ it's observed in tracer tests

Mixing ➔ dilution ➔ controls reactions

They are equated in conventional ADE



Effect on data



Sampling always causes mixing (sometimes huge)

Alternatives to ADE: MRMT, memory functions, CTRW, FDE,… (non-local)

View medium as consisting of two parts: mobile (f) and immobile (im)

$$\phi_f \frac{\partial c_f}{\partial t} = \nabla \cdot \left(D_f \cdot \nabla c_f \right) - q \cdot \nabla c_f + F_{im}$$

F_{im}: Exchange between f and im, given by

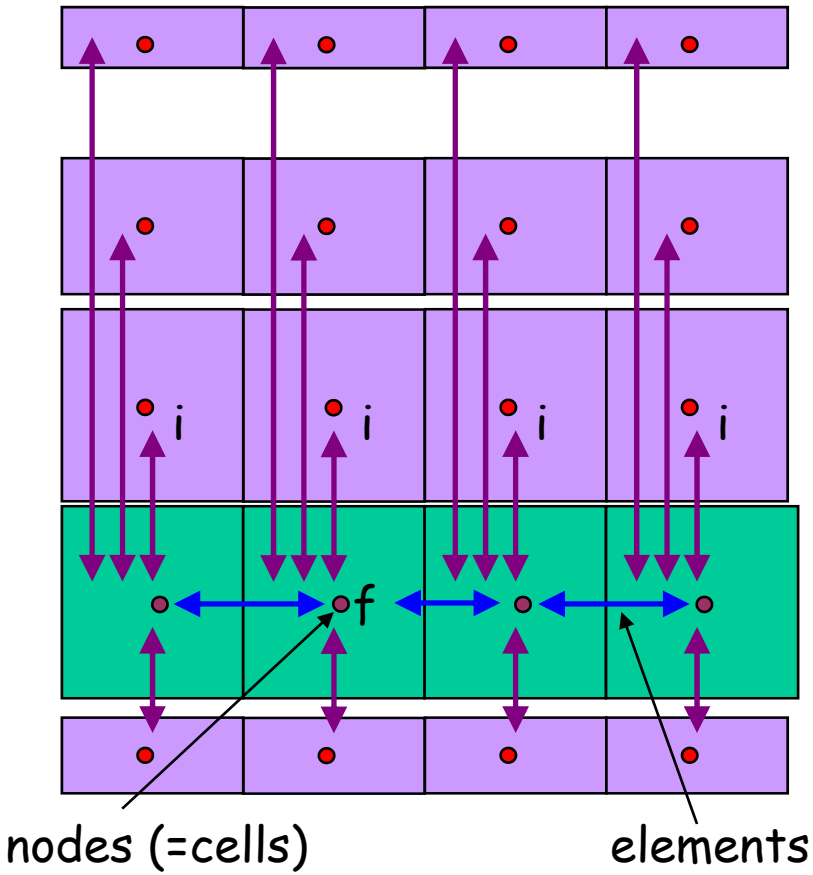
$$F_{im} = g * \frac{\partial c_f}{\partial t}$$

g: memory function, concept imported from leaky aquifer modelling (Herrera): can be viewed as

- Flux in response to unit change at boundary
- Residence time distribution in immobile region

Berkowitz, Dentz, Haggerty, Benson, LeBorgne… and a long etc, including yours truly

Physical and Numerical representation



This can be represented in two ways:

1) Having an appropriate mesh with nodes representing i
2) Eliminating i as an explicit unknown (expressing c_i as a function of c)

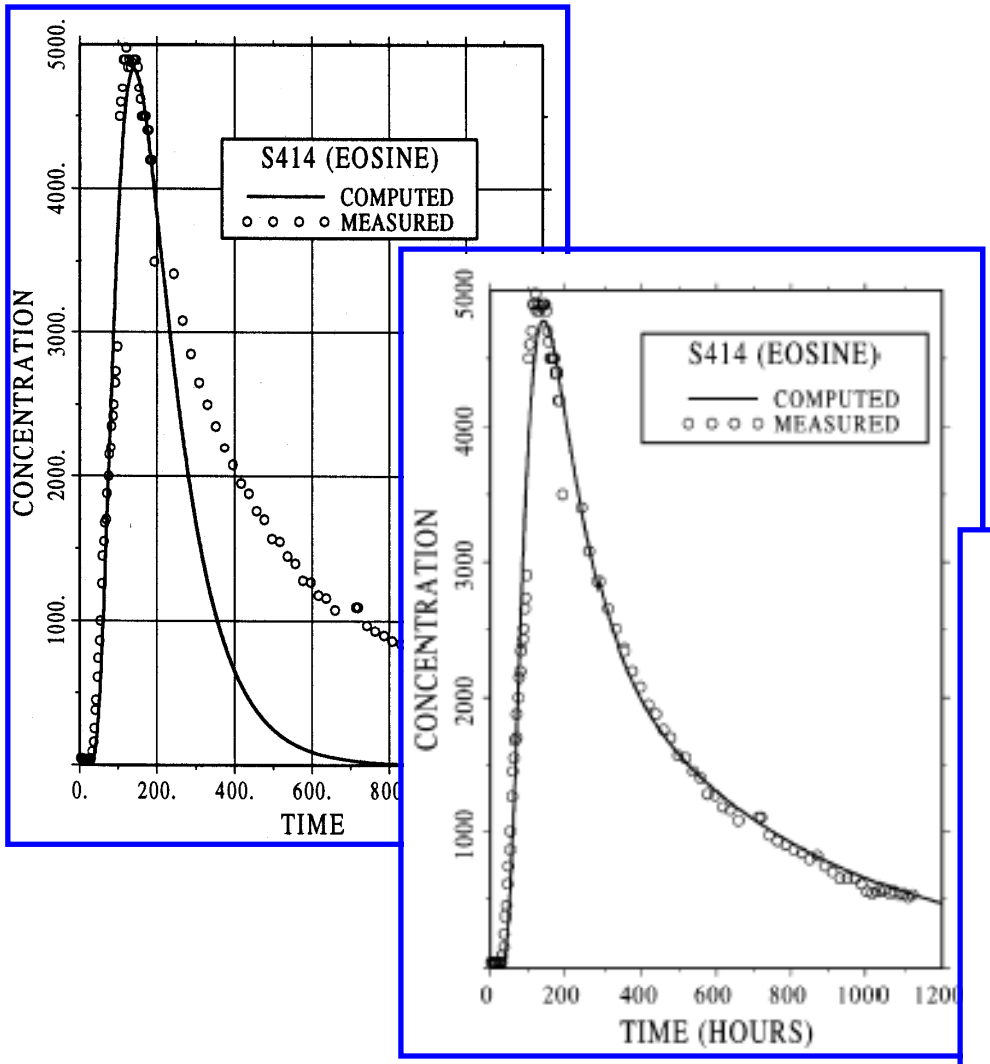
Mobile region transport (Diff)

Mobile region transport (ADE)

Mobile region transport (Diff)

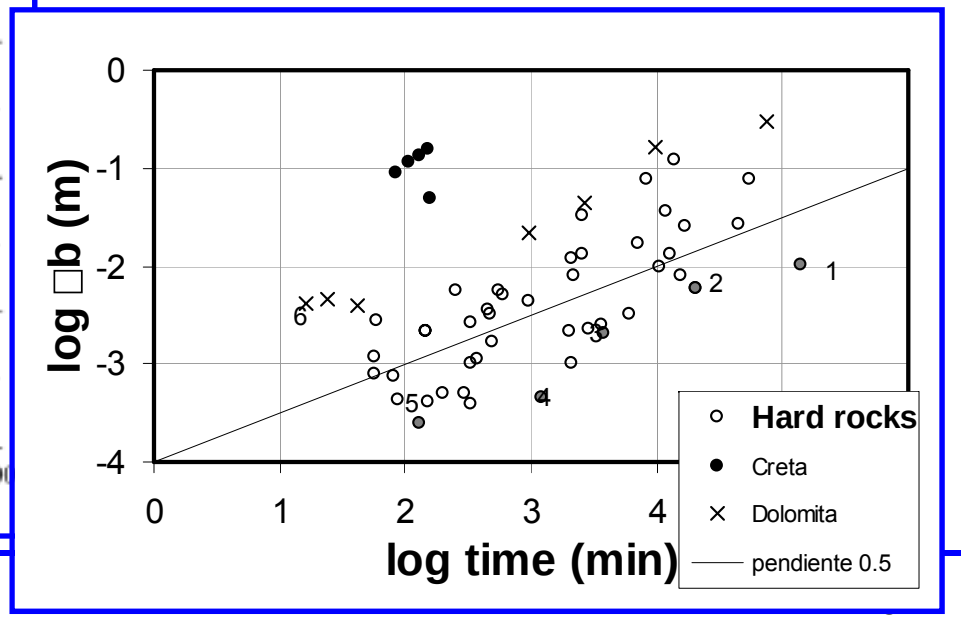
(Silva et al, 2009)

Non local formulations work for conservative transport



It explains not only tailing in BTC's,

but also time dependence of apparent porosity, etc



Testing the approach on simulated heterogeneous medium: two steps

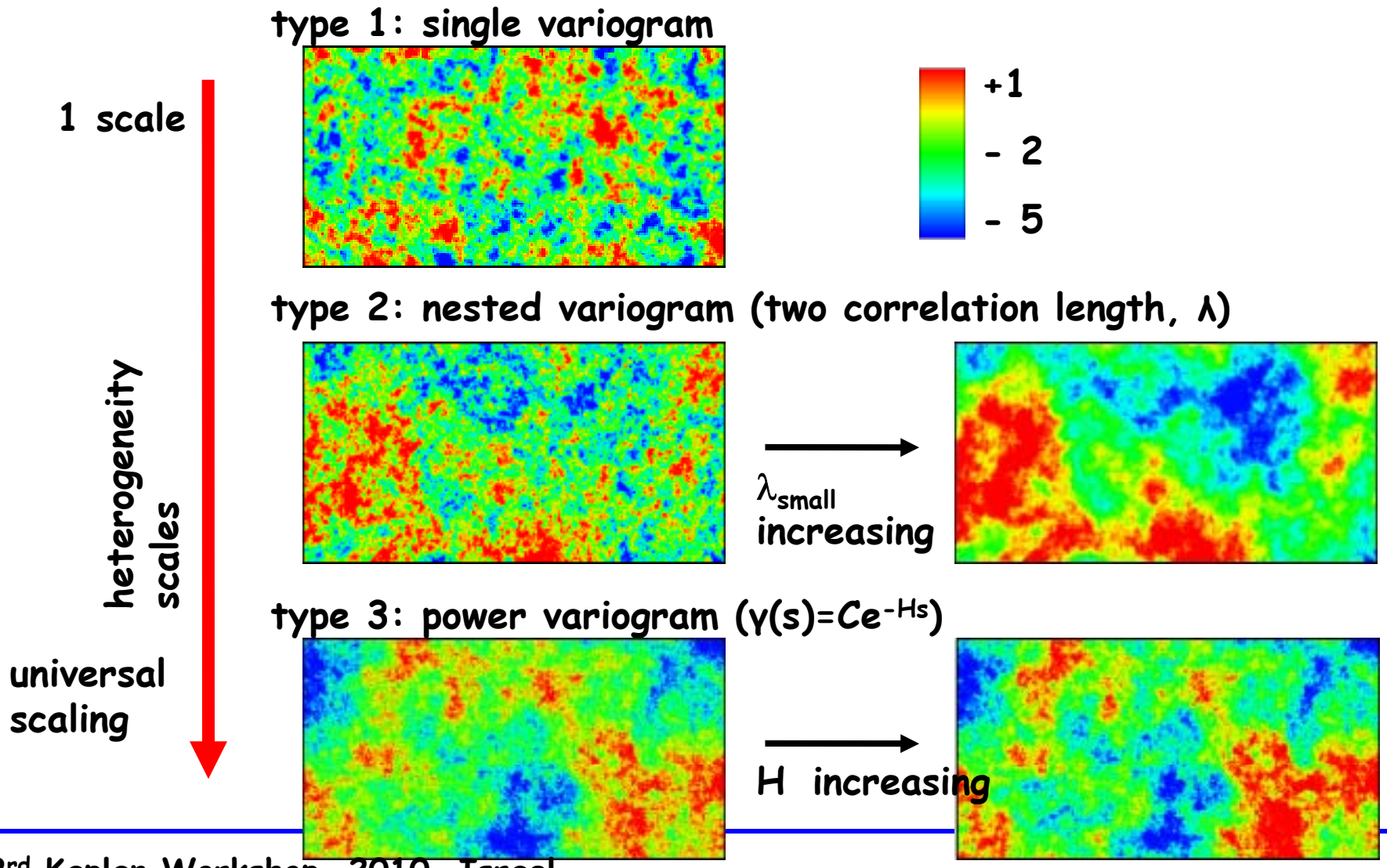
Conservative transport characterization

1) Generate heterogeneous medium
2) Simulate conservative transport
3) Compute BTC's
4) Find memory function (Willmann et al, 2008)

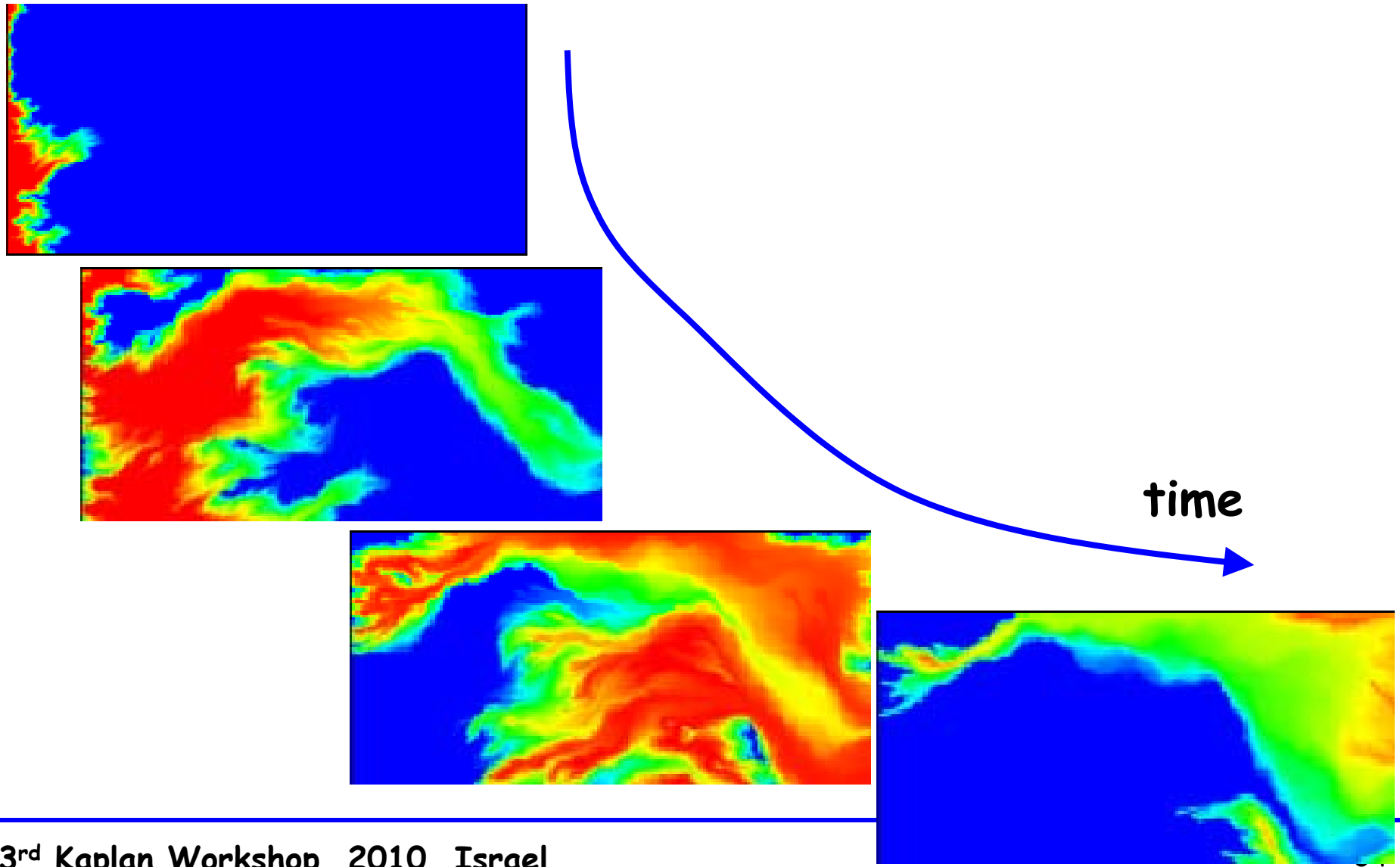
Reactive transport simulation

1) Simulate reactive transport of binary system with an equilibrium dissolution precipitation reaction **on the heterogeneous medium**
2) Simulate reactive transport using above memory function and proposed approach
3) Compare (Willmann et al, 2010)

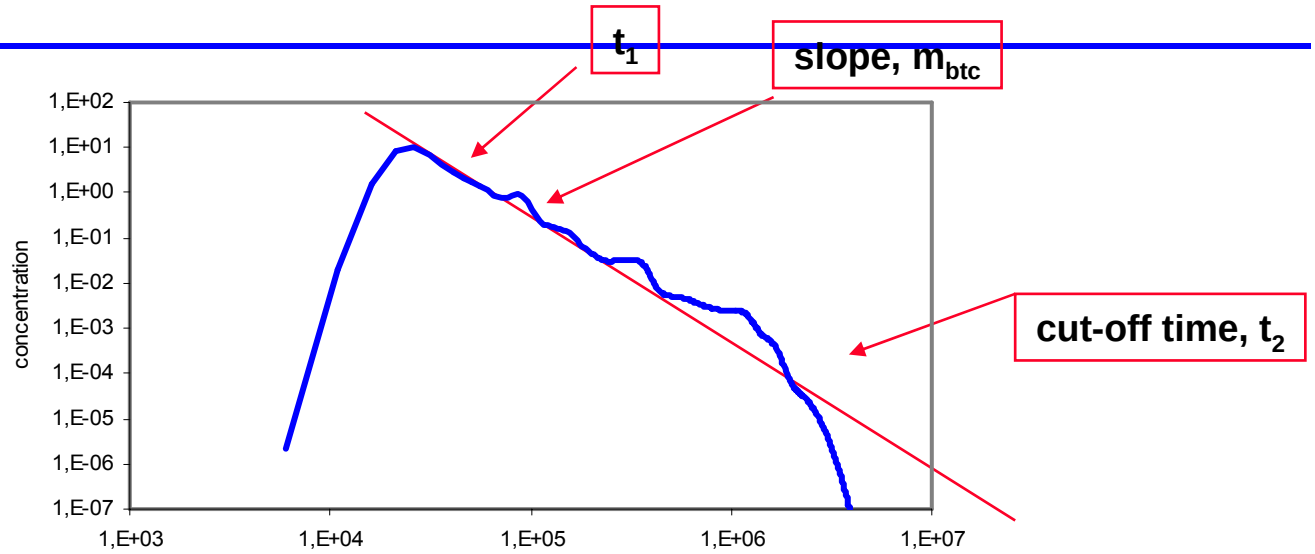
Generate heterogeneous medium

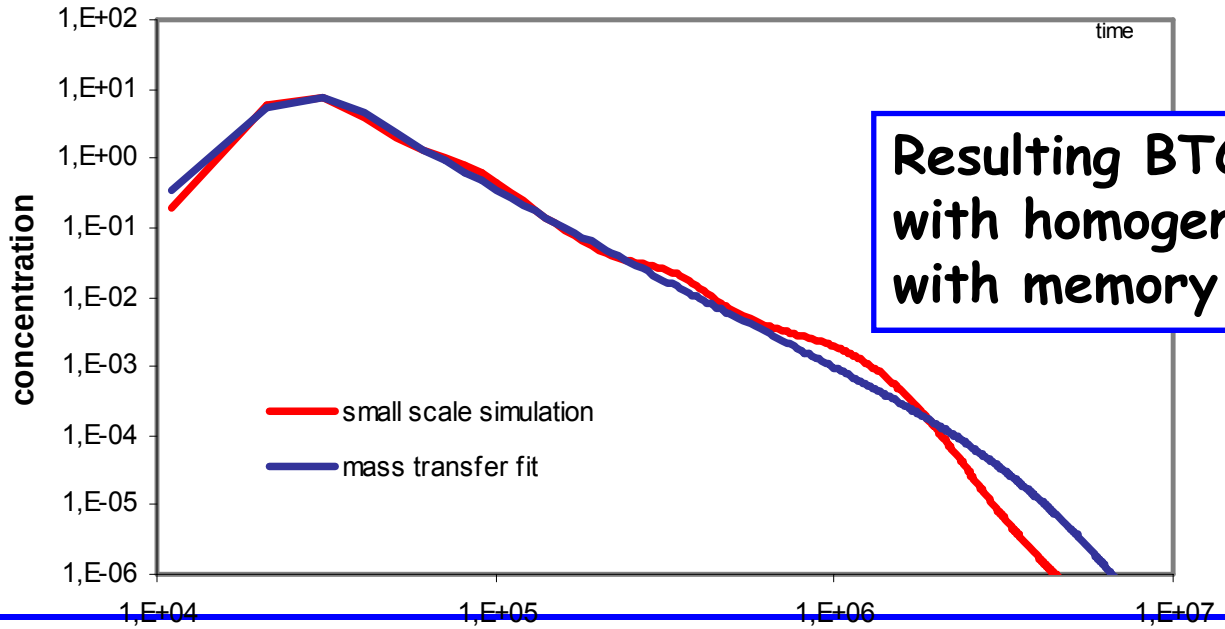


Simulate transport



Analyze BTC's





Resulting BTC's can be obtained with homogeneous 1D transport with memory function

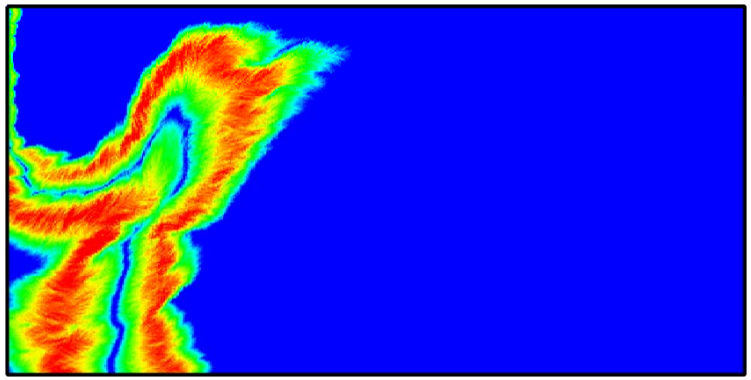
Results reactive - transport:

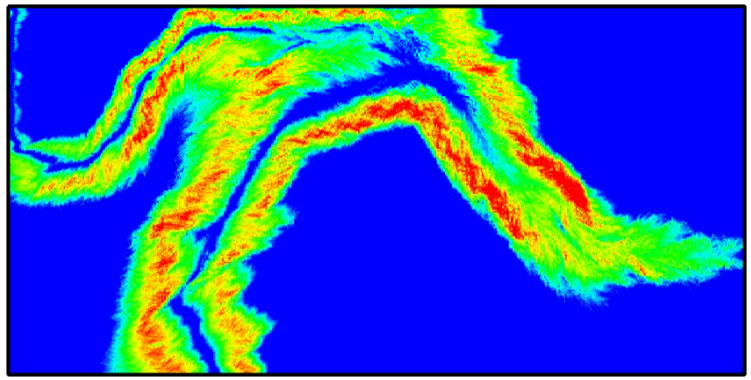
2D simulations: Reaction rates

reaction rates

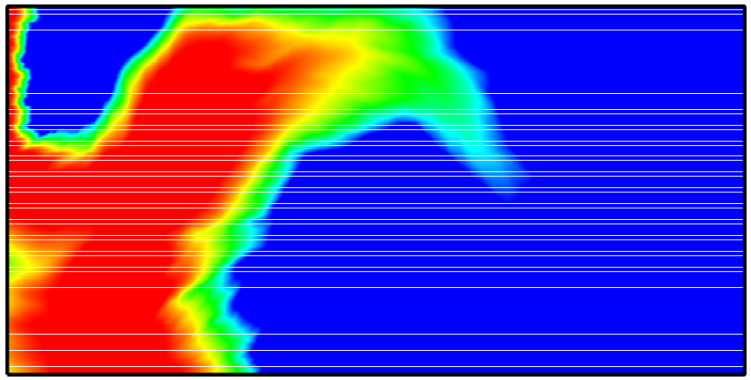
time 1

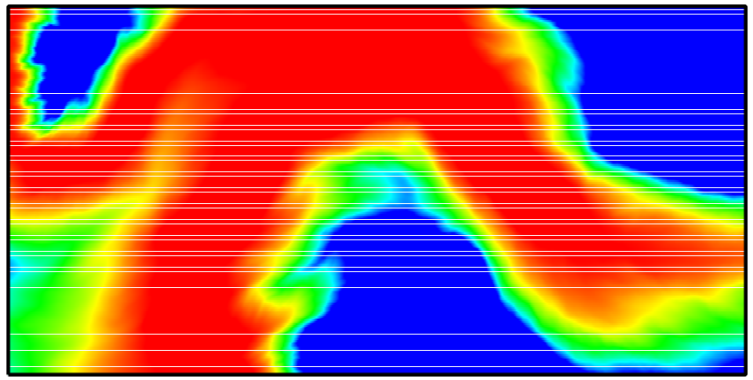
time 2





component u

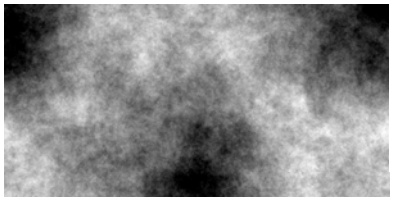


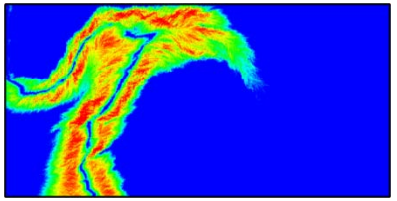


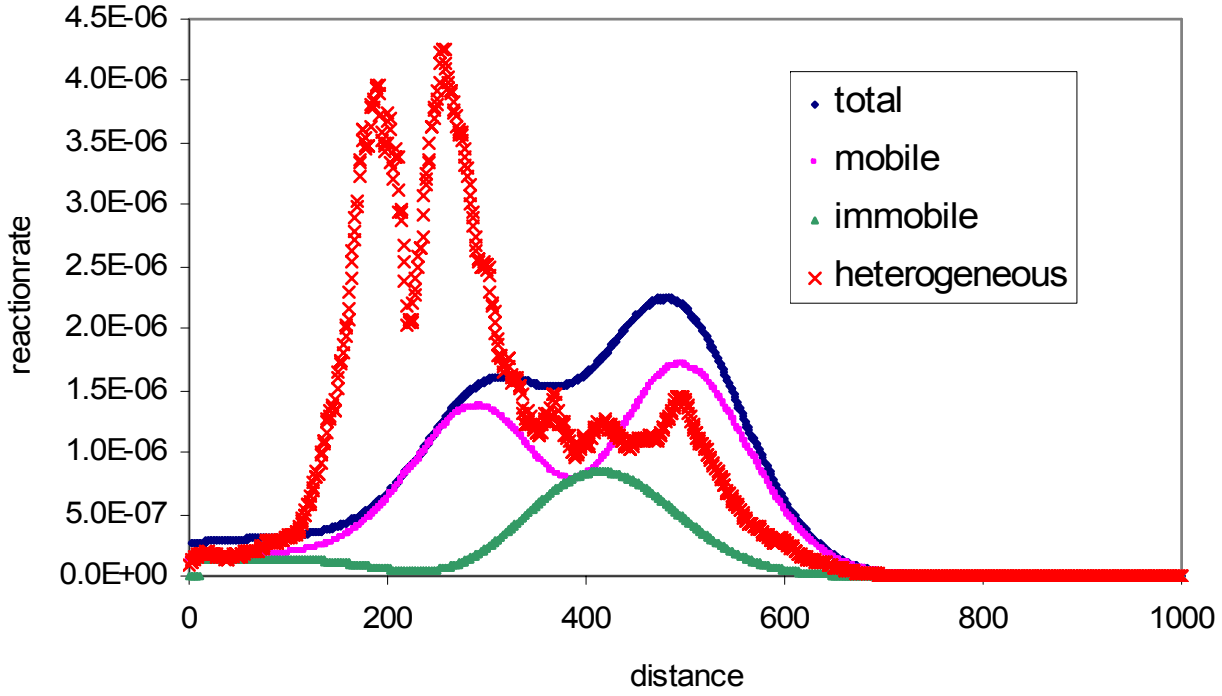
Results - reactive transport:

Reaction rates

Comparison between heterogeneous and MRMT model

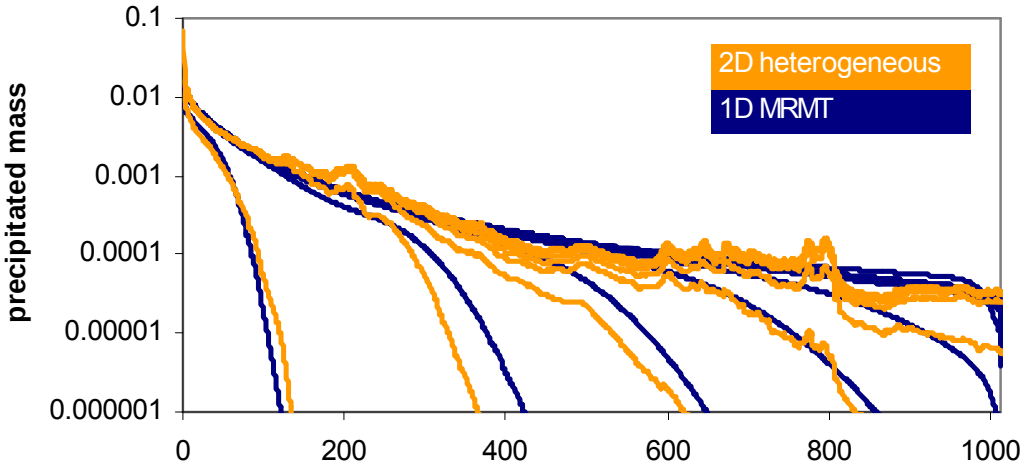




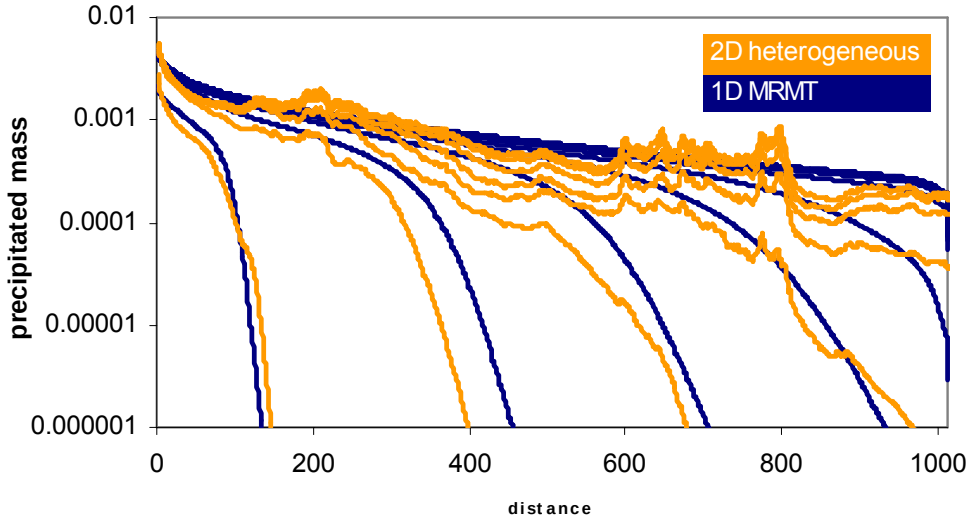


Results - reactive transport:

Total precipitated mass



K=0.01



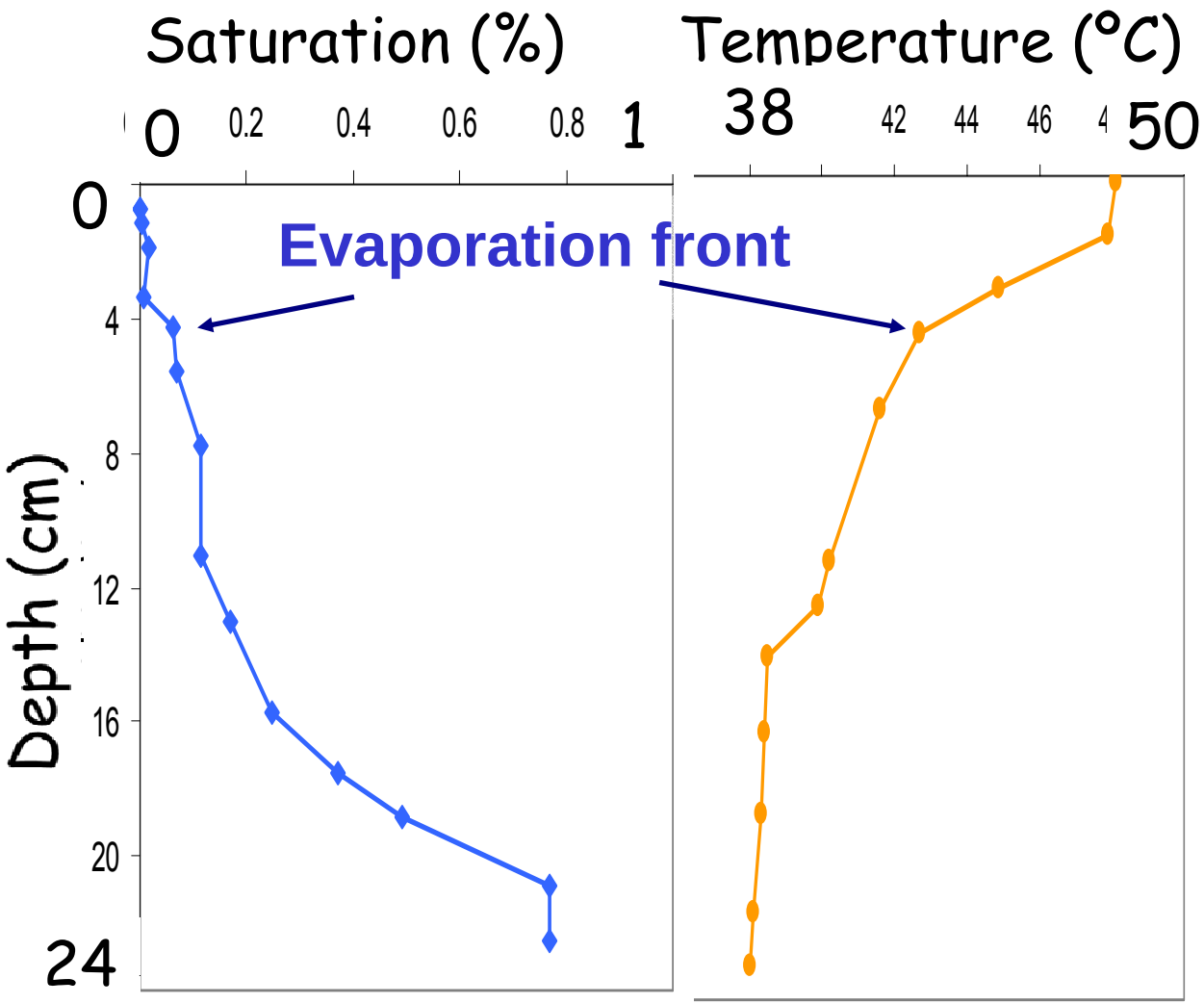
K=0.0001

3rd (and final) conclusion

- We do not really know how to simulate mixing, but spreading
- Non-local models separate mixing and spreading
- Their parameters can be linked to the underlying heterogeneity.
- Excellent agreement between 2D heterogeneous and 1D MRMT solutions in terms of total precipitated mass.

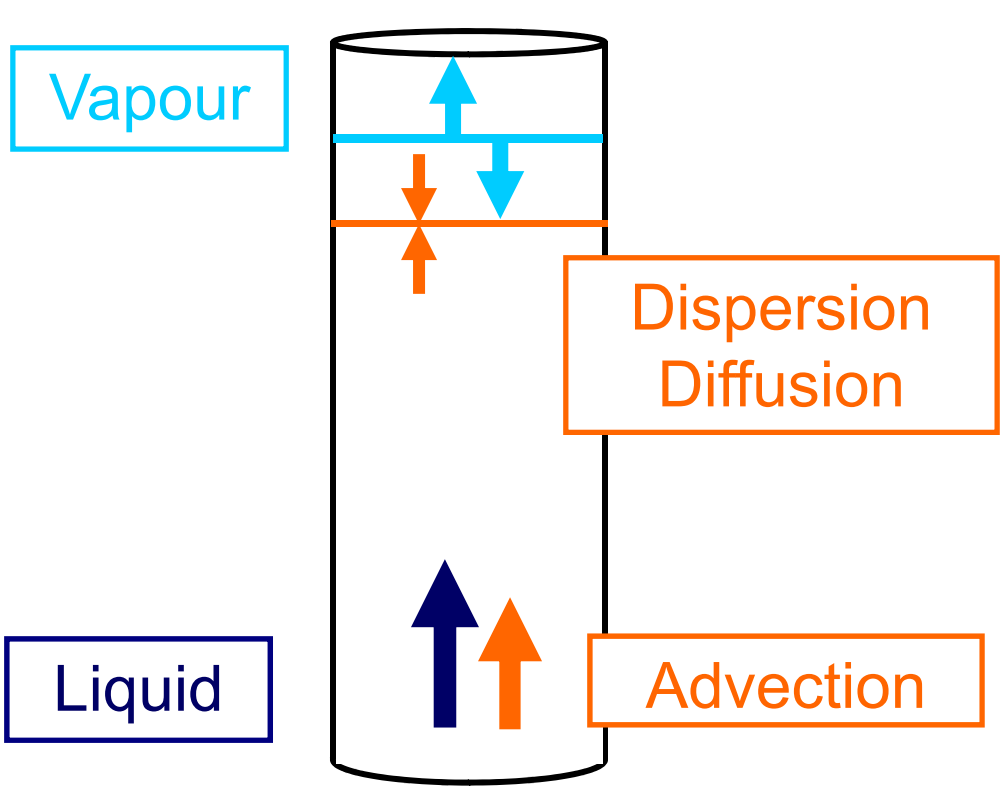
Salinization by Evaporation

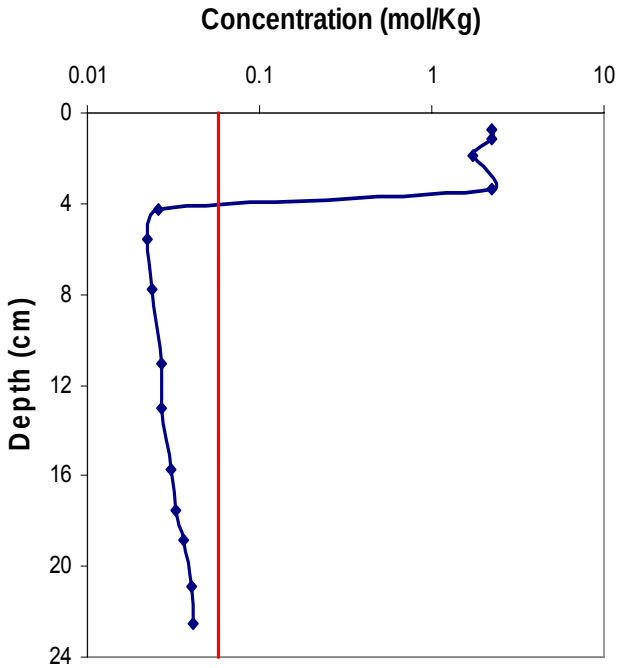
Initially water saturated (low $MgSO_4$ conc)



(Gran et al, submitted)

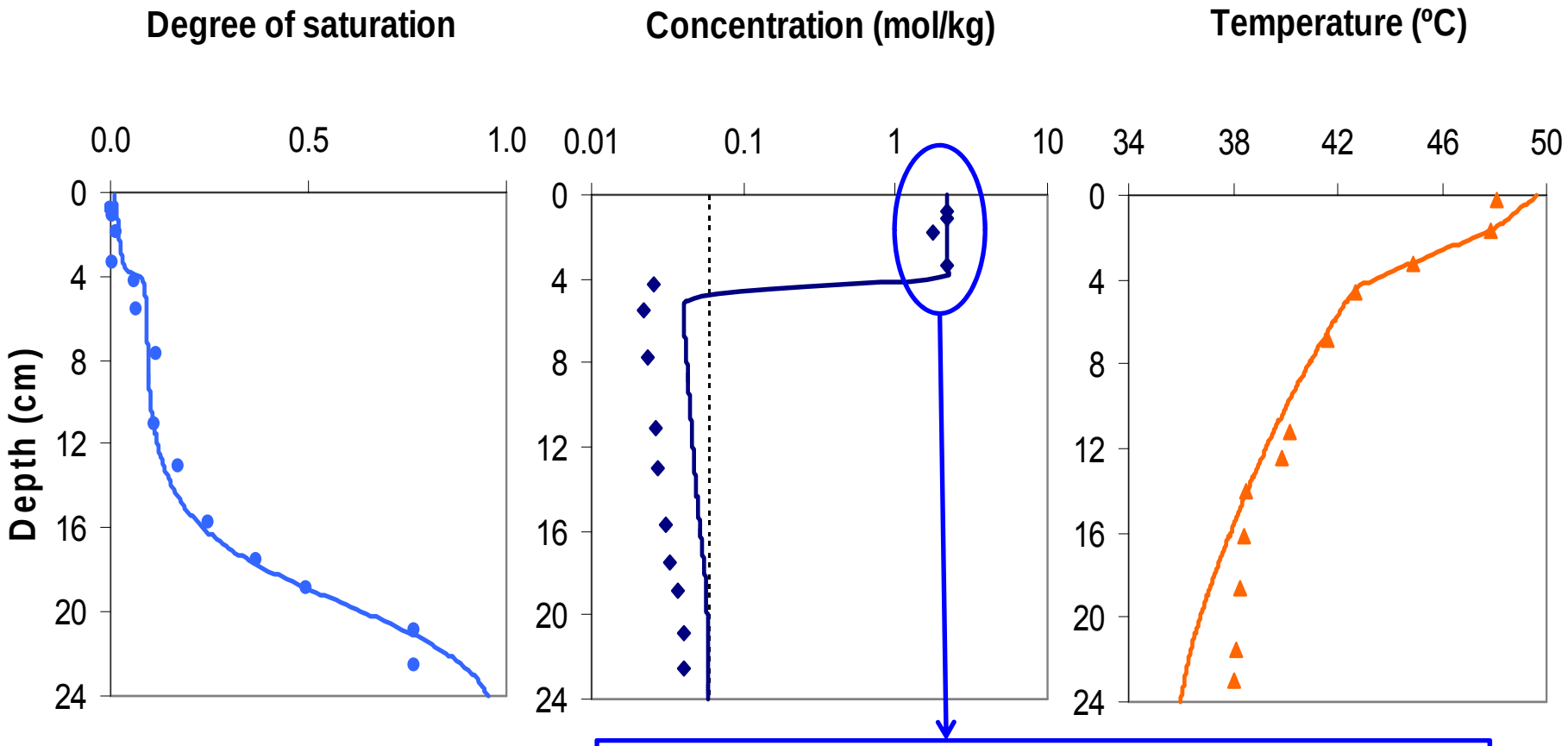
CONCEPTUAL AND NUMERICAL MODELING





1D model coupling multiphase flow & reactive transport using CodeBrightRetraso code Saaltink et al (2004). Chemistry with CHEPROO (Bea et al, 2010).

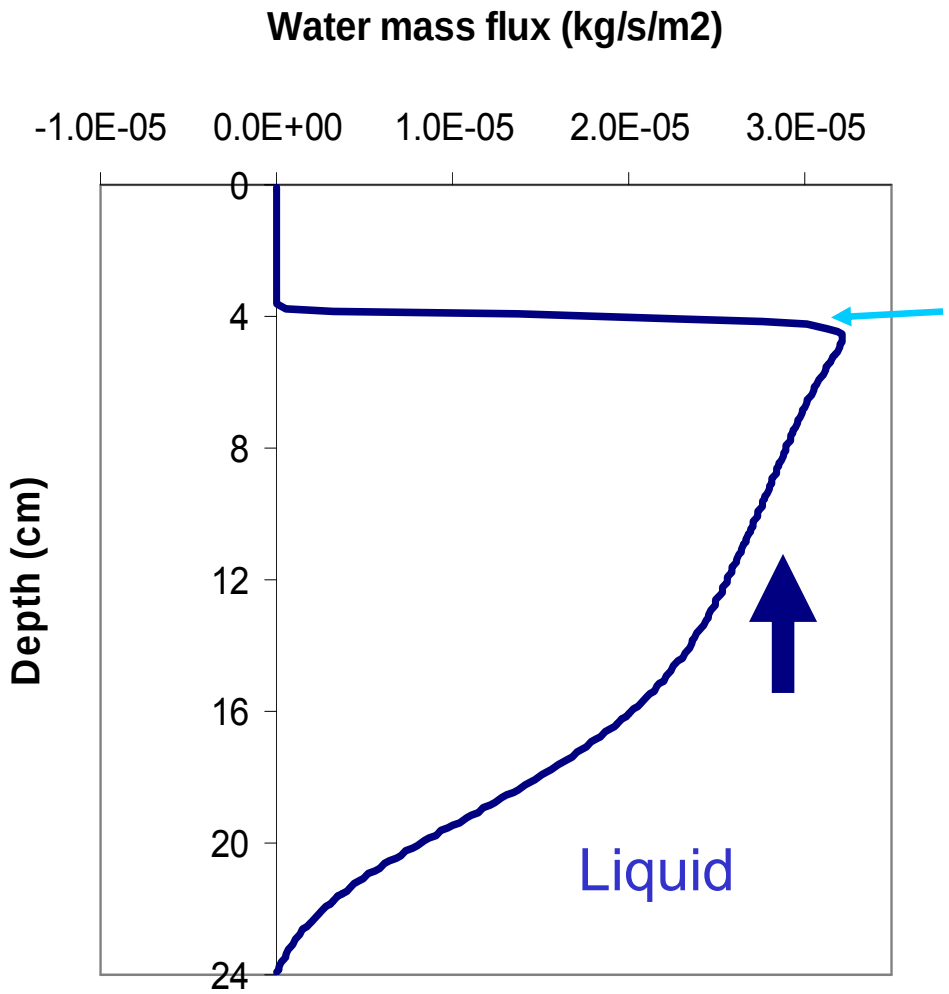
Model results (line) and measurements (dots)



Top: Pentahydrite $MgSO_4 \cdot 5H_2O$

Bottom: Epsomite $MgSO_4 \cdot 7H_2O$

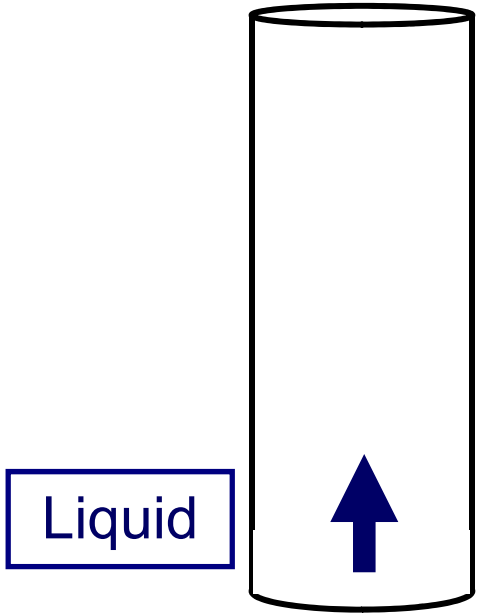
Results: Water flux



Positive value → Upward flux

Neg. value → Downward flux

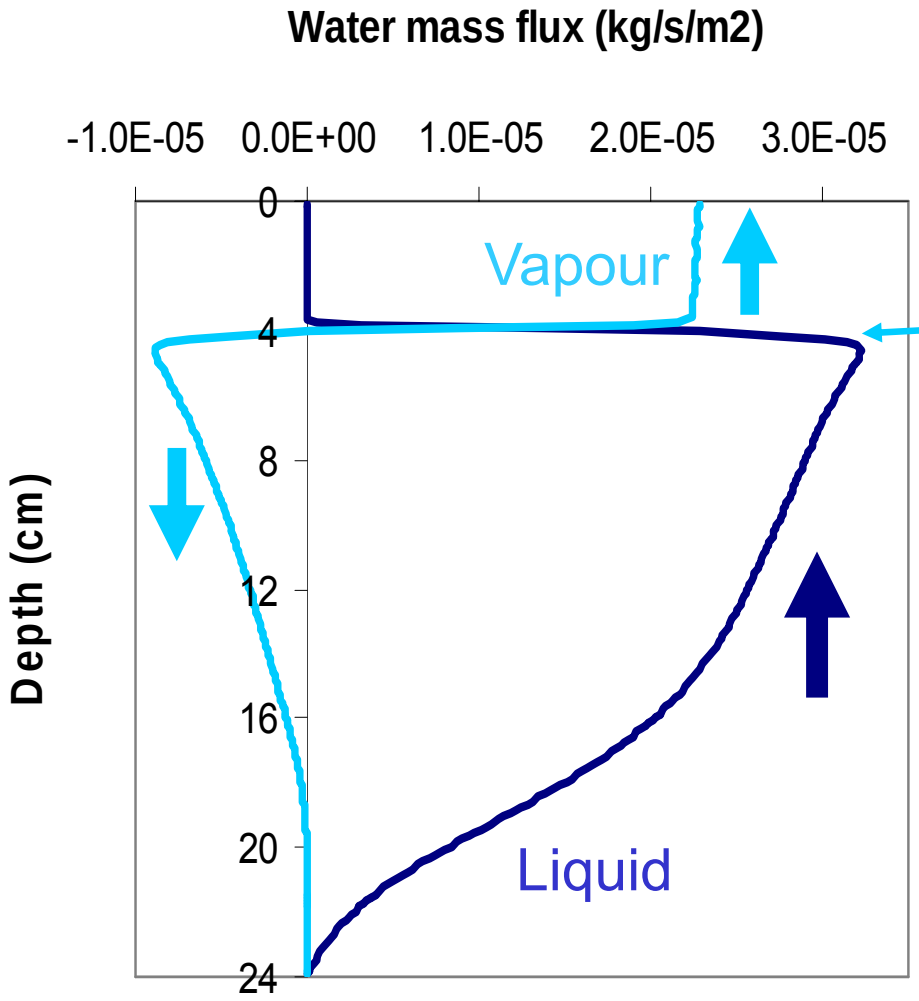
Evaporation front



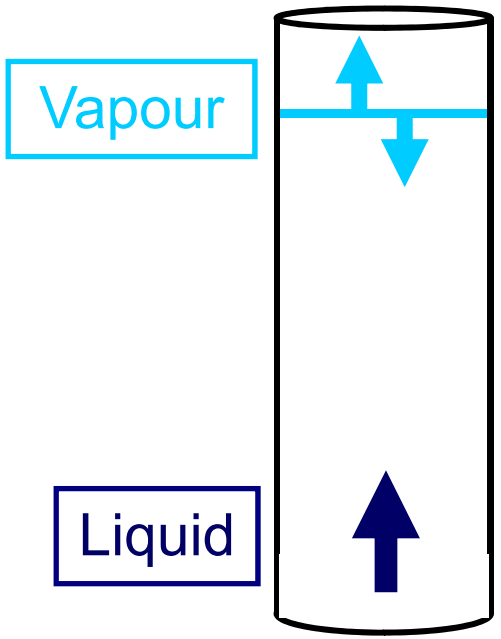
Results: Water flux

Positive value → Upward flux

Neg. value → Downward flux



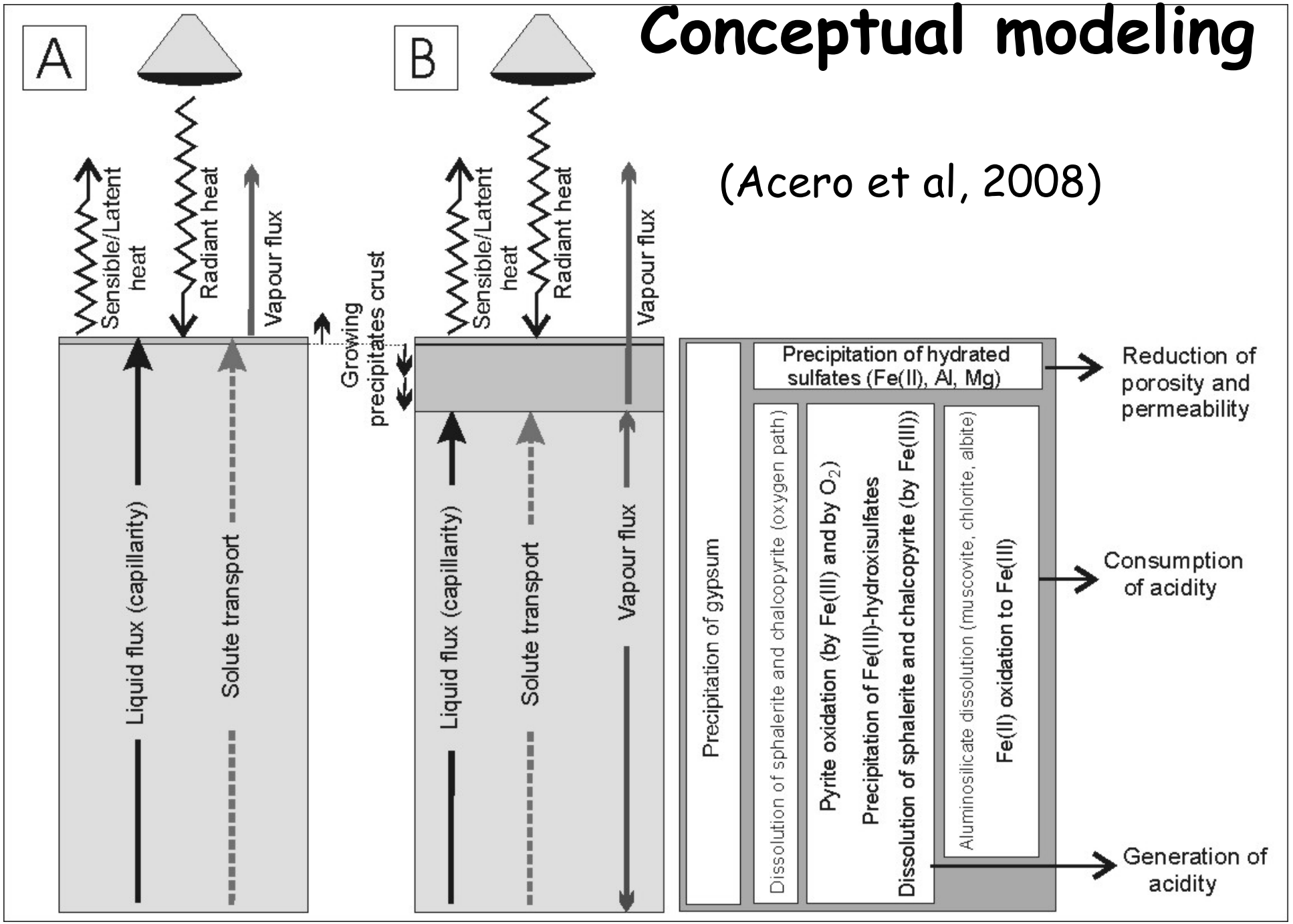
Evaporation front



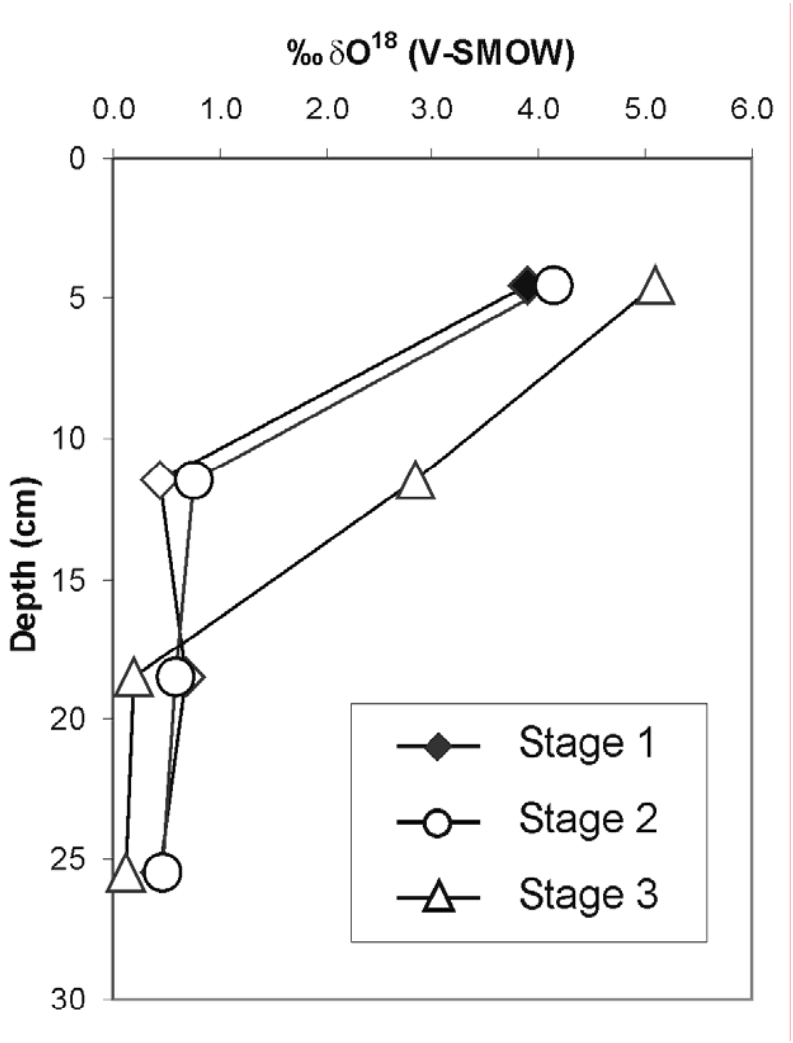
Similar experiments acid generation from mine tailings

Conceptual modeling

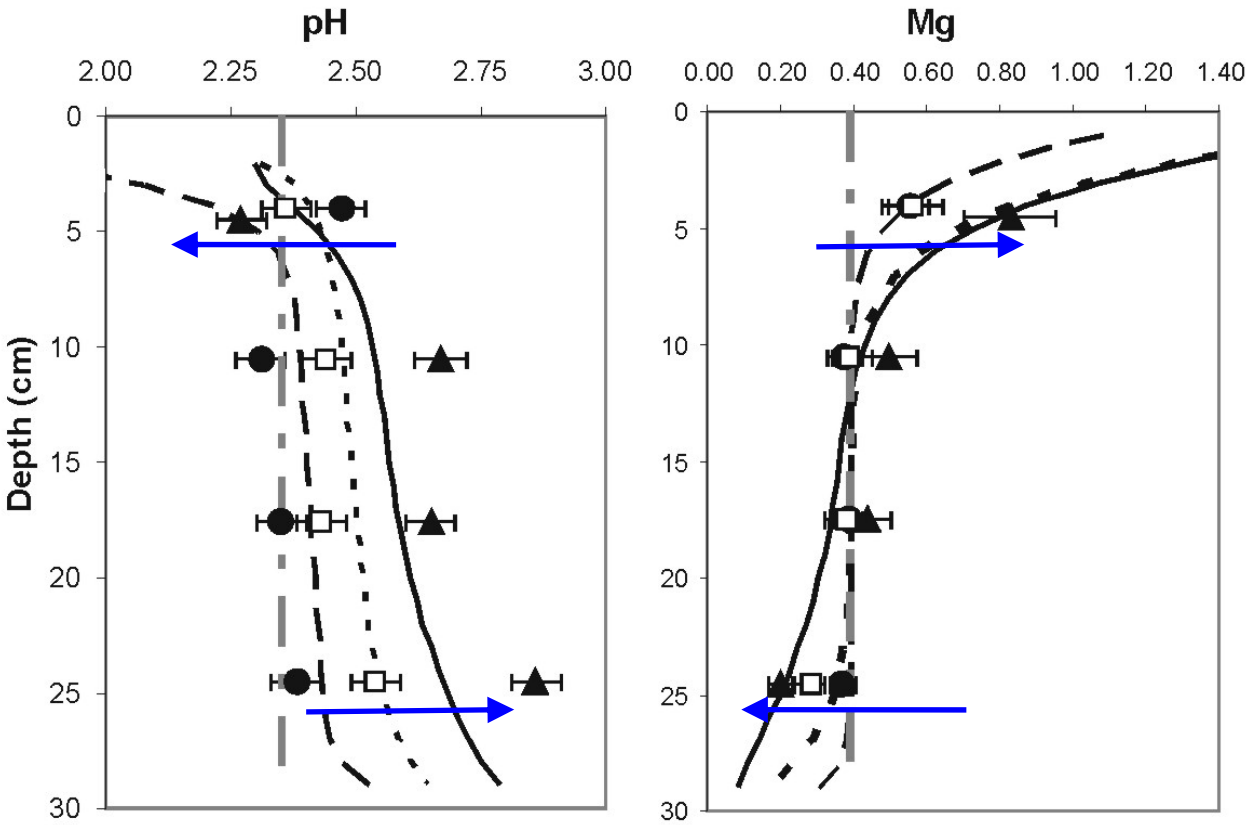
(Acero et al, 2008)

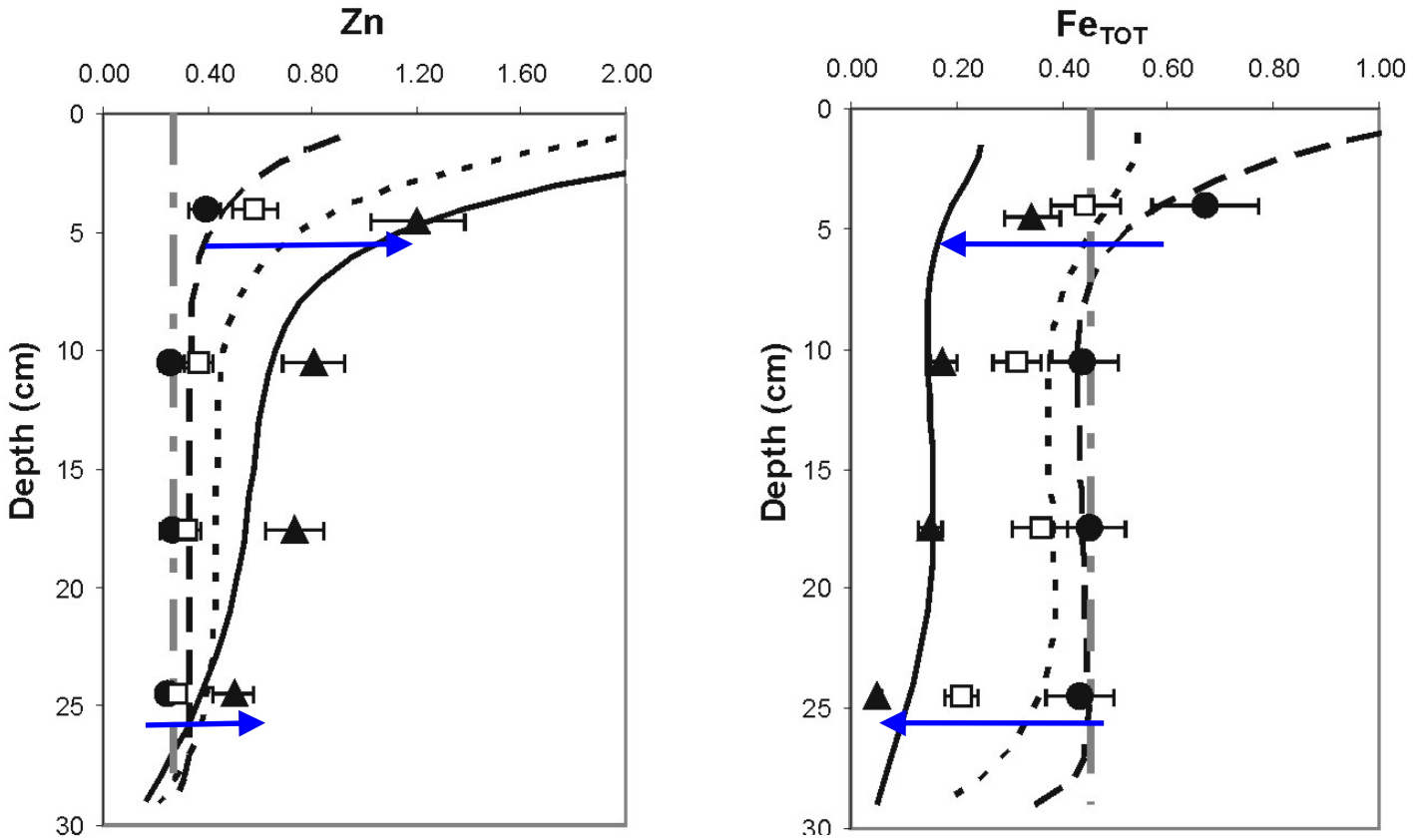


Water isotopes confirm condensation below



Types of behaviour of solutes




Zn
0.00
0.40
0.80
1.20
1.60
2.00
Depth (cm)
0
5
10
15
20
25
30
Fe$_{TOT}$
0.00
0.20
0.40
0.60
0.80
1.00
Depth (cm)
0
5
10
15
20
25
30

Summary

- Is Reactive transport needed?
  - Equilibrium reactions (rate , where, when, under which conditions) are controlled by transport.
  - Applications probably required to help understand complex interactions
- Can it be understood?
  - All it takes is to understand components
  - The difficult part is to choose the relevant species and reactions.
- Can be solved efficiently?
  - Yes, very often (but not always!)

But

Reactions are driven by **disequilibrium**

Disequilibrium is driven by **actual mixing**

We need to know how to evaluate actual mixing!

We are working on it!