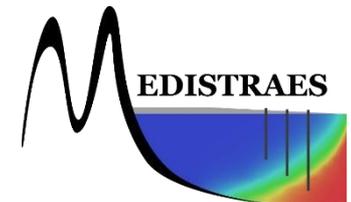
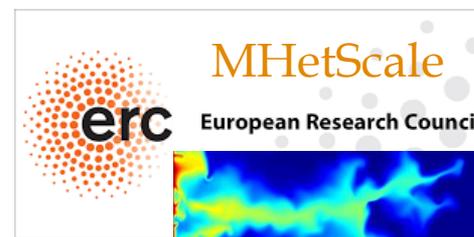


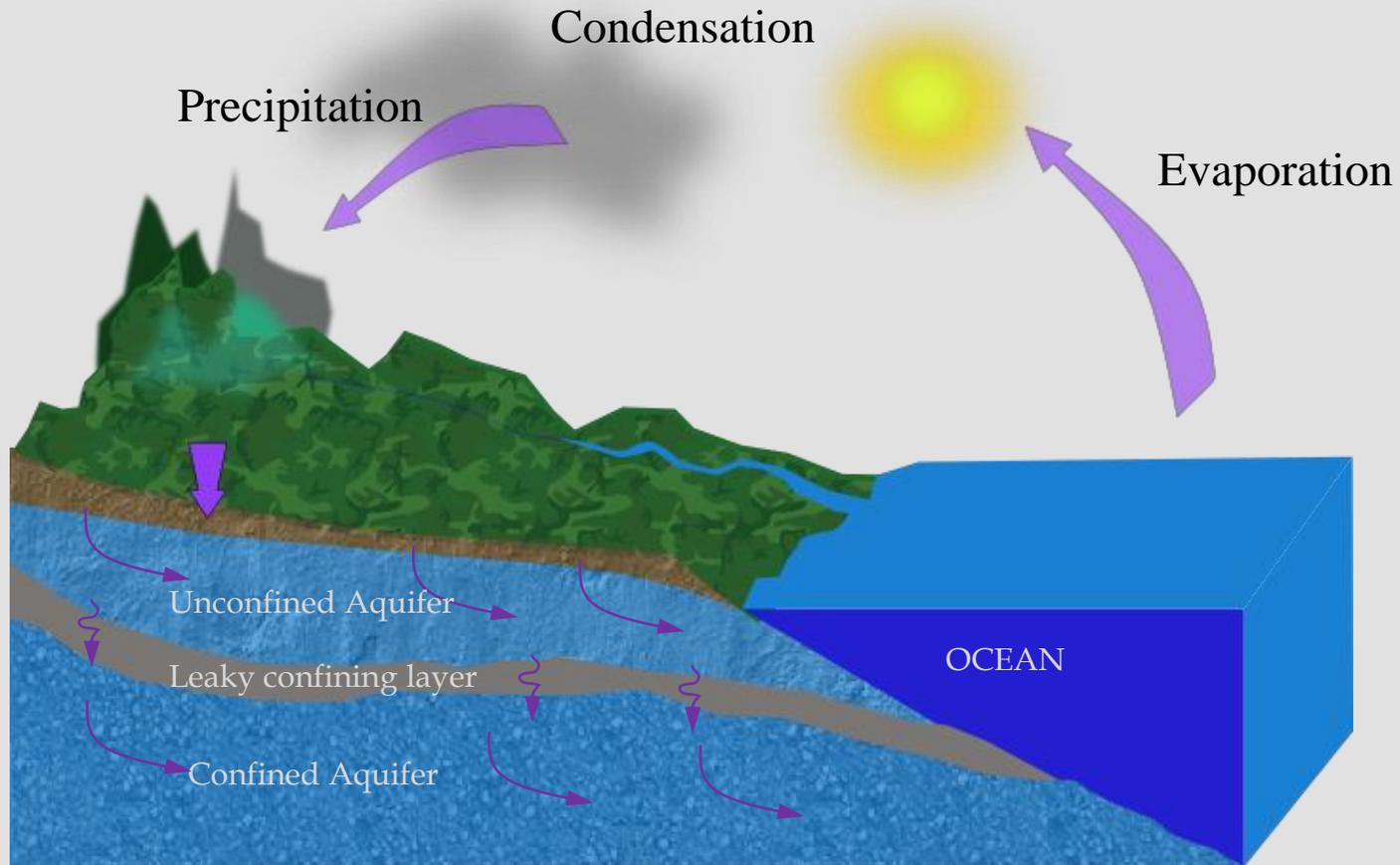
# Seawater Intrusion

Maria Pool (1,2)

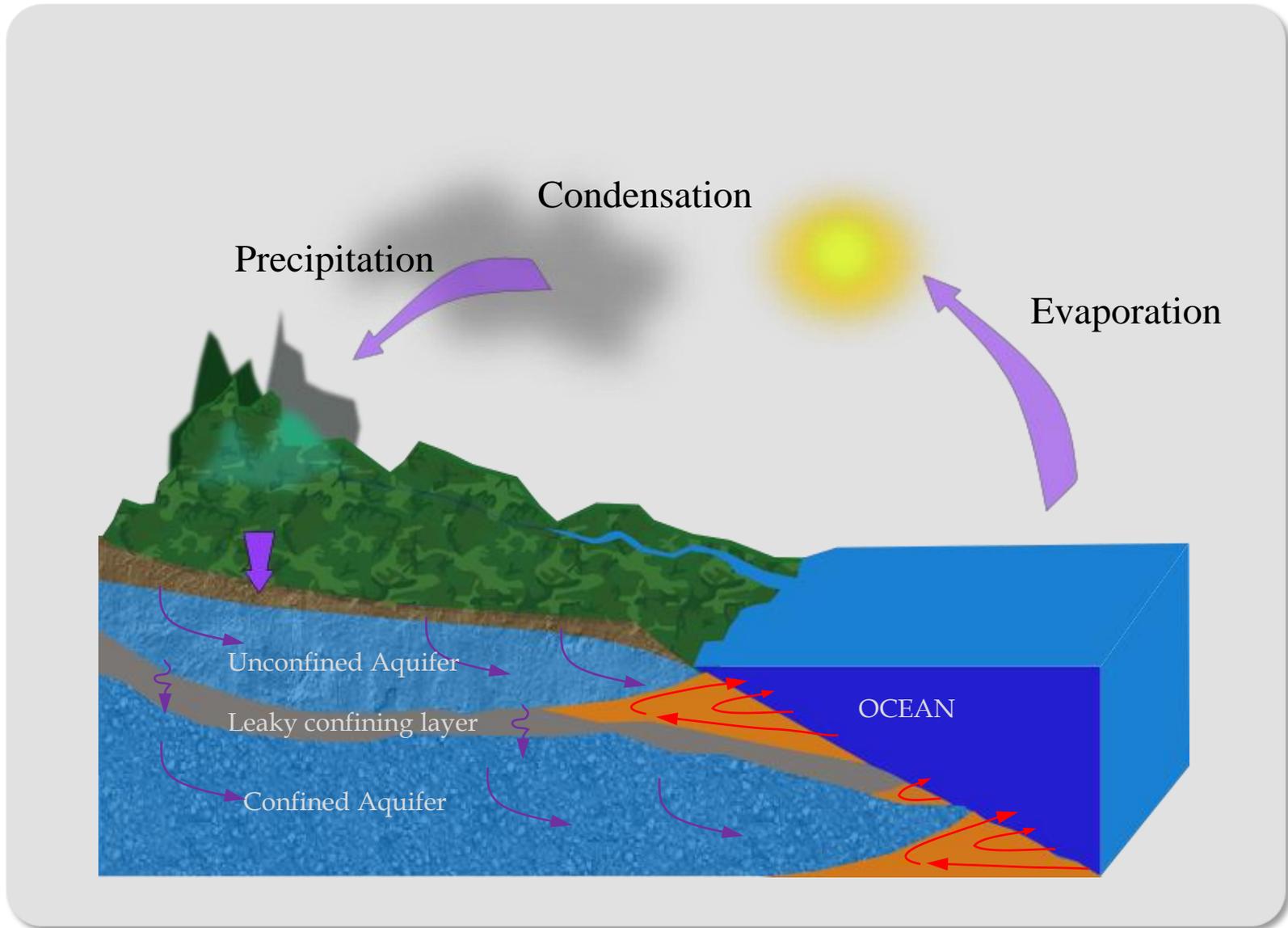
(1) Spanish National Research Council (IDAEA-CSIC), Barcelona, Spain,  
(2) Associated Unit: Hydrogeology group (UPC-CSIC)



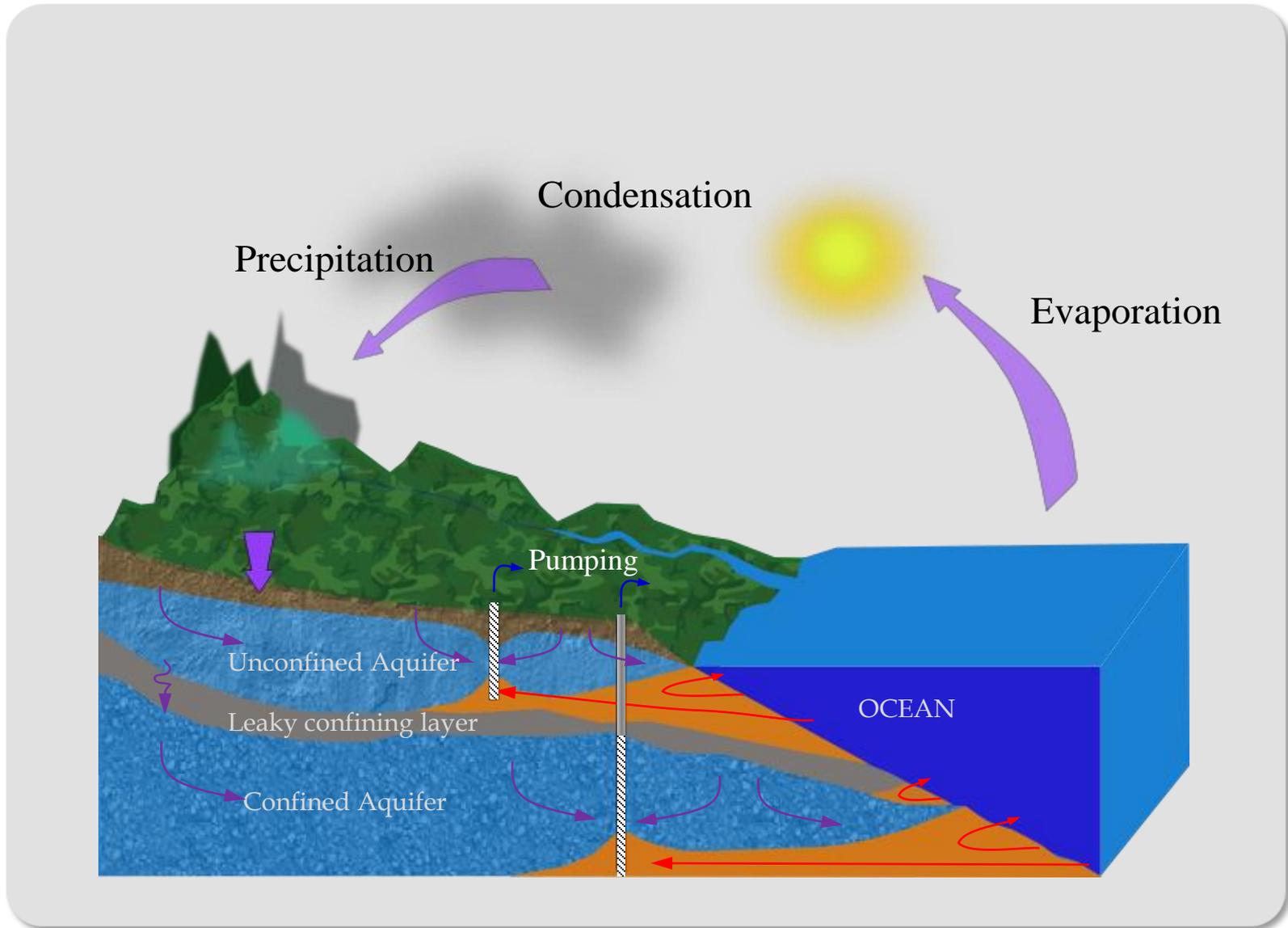
# What is Seawater Intrusion?



# What is Seawater Intrusion?



# What is Seawater Intrusion?

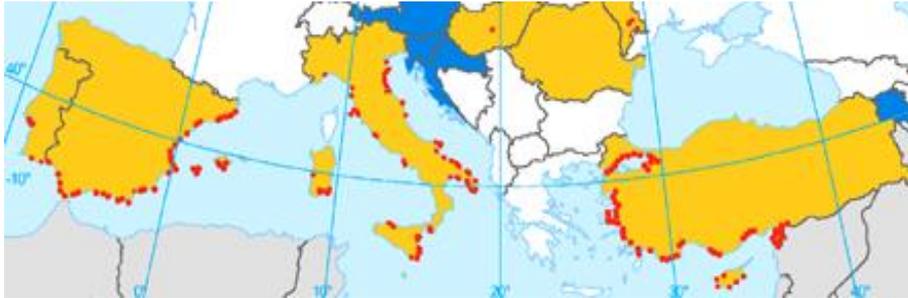


# Why is Seawater Intrusion a problem?

---

- About 70% of the world population lives in coastal areas [Bear and Cheng, 1999].
- Seawater intrusion has caused significant losses in valuable water resources and in agricultural production globally [FAO, 1997].

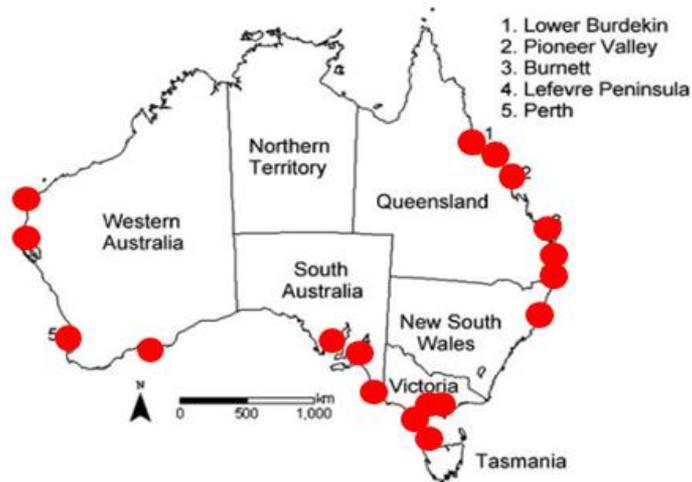
# Global Problem



European Environmental Agency. For a detailed account of SWI in Europe, see E. Custodio [2010] *Hydrogeology Journal* 18 (1)



The Center of Advanced Materials for the Purification of Water with Systems



Werner AD (2010) , *Hydrogeology Journal* 18 (1): 281-285.



E. Bocanegra et al [2010]. State of knowledge of coastal aquifer management in South America *Hydrogeology Journal* 18 (1):

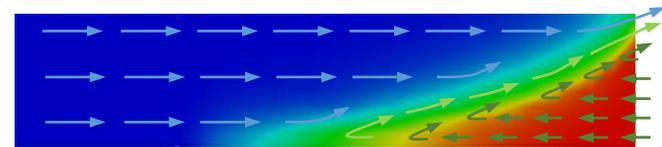
# Dealing with seawater intrusion problems

- Seawater intrusion is a complex three-dimensional phenomenon governed by coupled non-linear equations that describe density dependent ground water flow and solute transport.

## Equations

$$\mathbf{u} = -\rho K \cdot \left[ \nabla h + \epsilon \left( \frac{\omega}{\omega_s} \right) \hat{e}_g \right]$$
$$\frac{\partial(\rho\phi\omega)}{\partial t} = \nabla \cdot (\mathbf{u}\omega) - \nabla \cdot (\mathbf{D}\nabla\omega)$$
$$\rho = \rho_f \left( 1 + \epsilon \left( \frac{\omega}{\omega_s} \right) \right)$$

density-dependent flow  
modeling

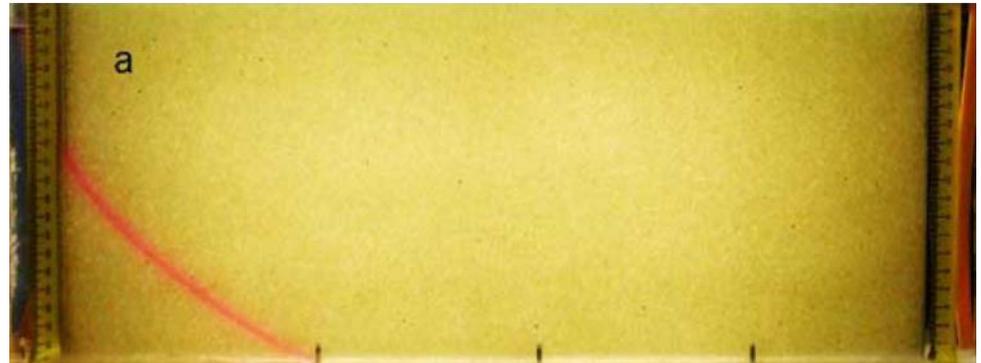
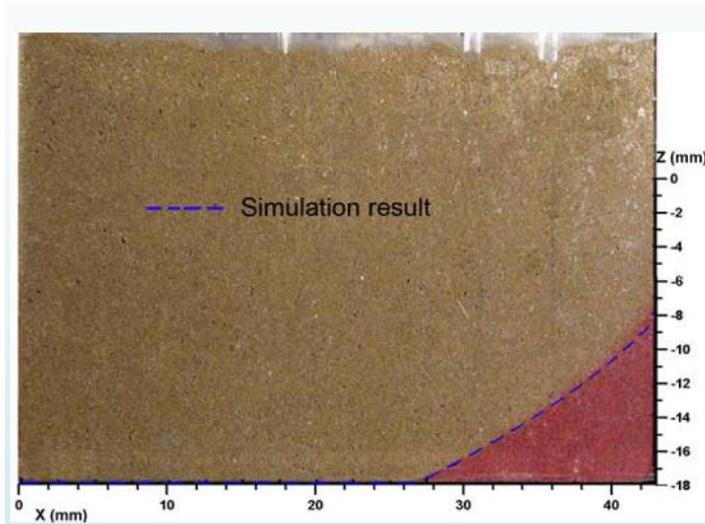


Inland

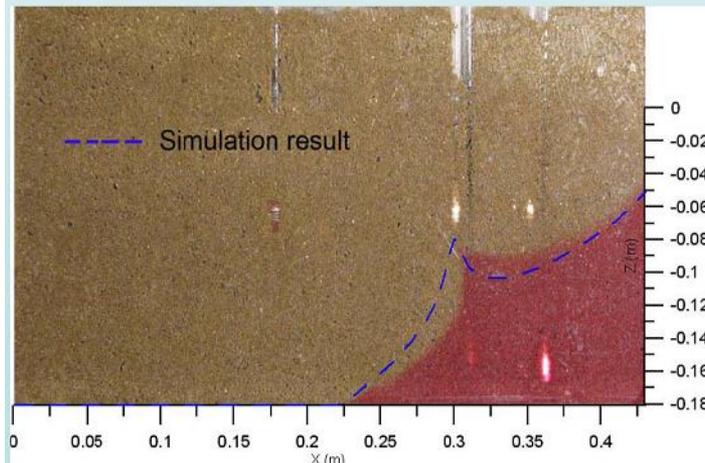
Sea

# Width of the mixing zone

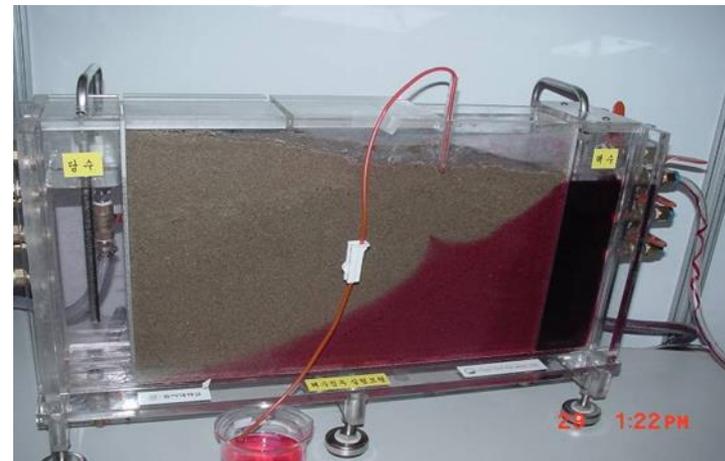
LABORATORY EXPERIMENTS suggest narrow mixing zones



E. Abarca and T. P. Clement (2009)



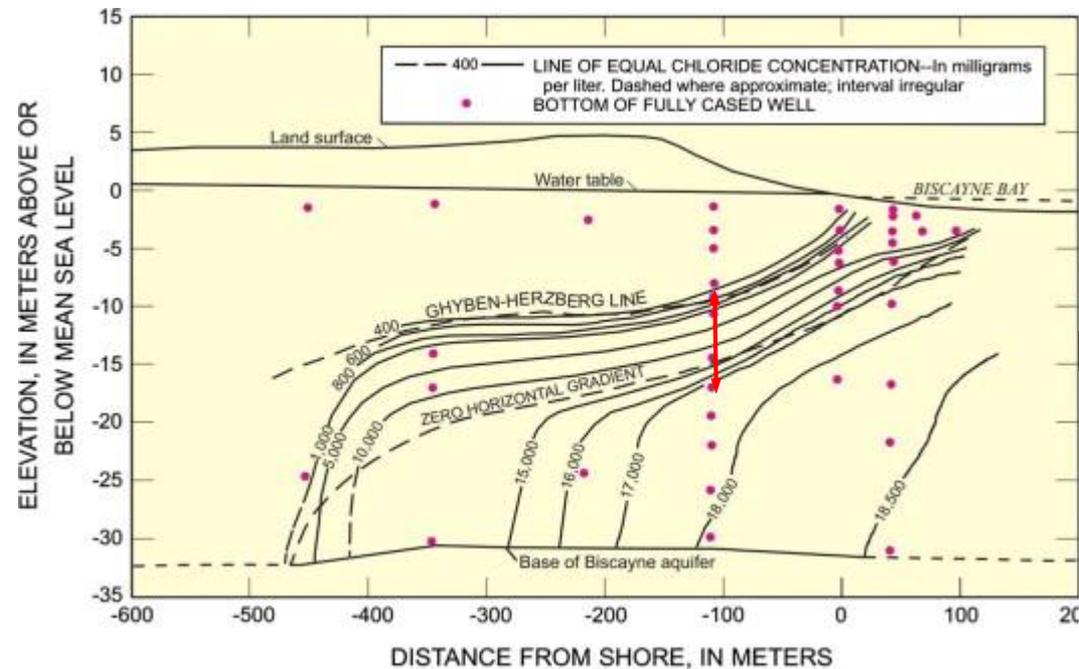
Park, N.S., S.H. Hong, L. Shi, K.S. Seo, and L. Cui. 2006.



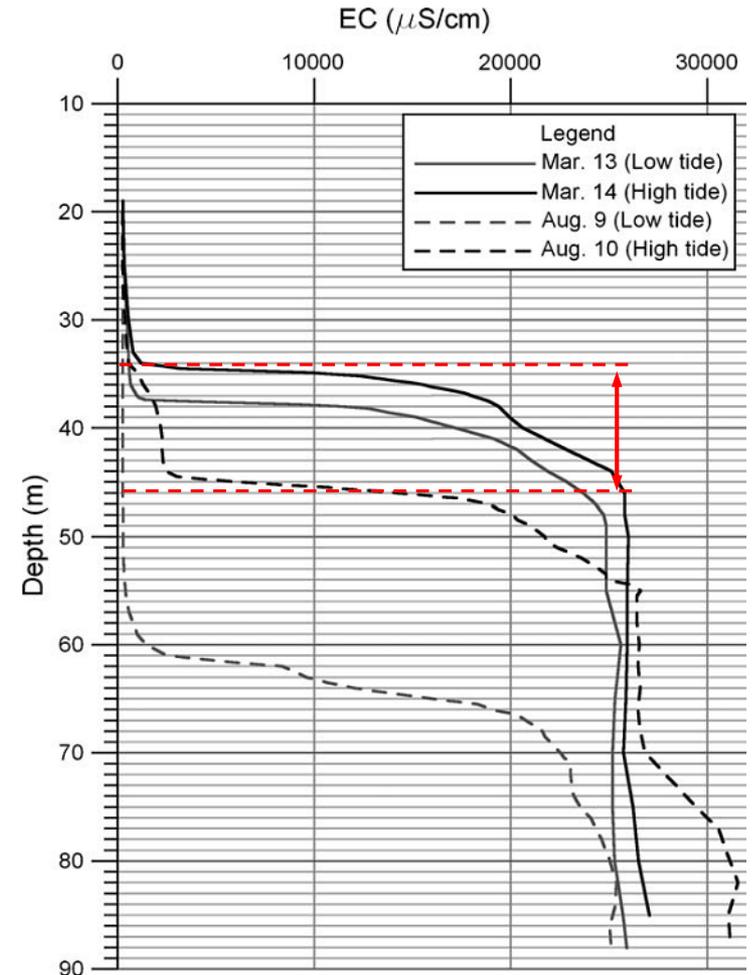
N. Park, S. Kim, and L. S. Dong (2008)

# Width of the mixing zone

FIELD MEASUREMENTS suggest very wide mixing zones



Langevin (2003)



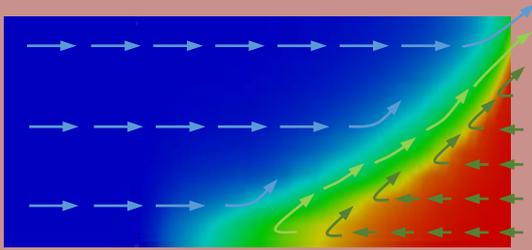
Kue-Young Kim, (2007)

Effects of periodic temporal fluctuations and  
fluid density effects on mixing and chemical  
reactions in coastal aquifers:  
Karst Formation

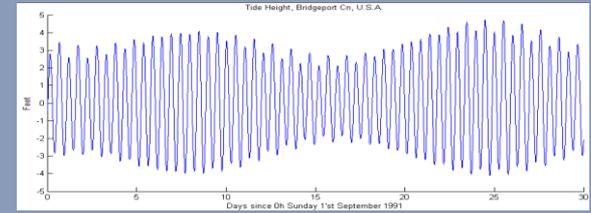


# COASTAL AQUIFERS: Processes

Density variations



Temporal Fluctuations  
Transient effects

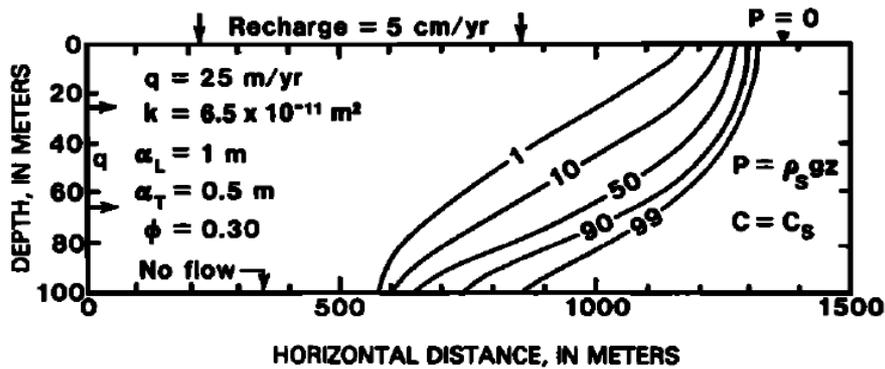


DISPERSION AND MIXING

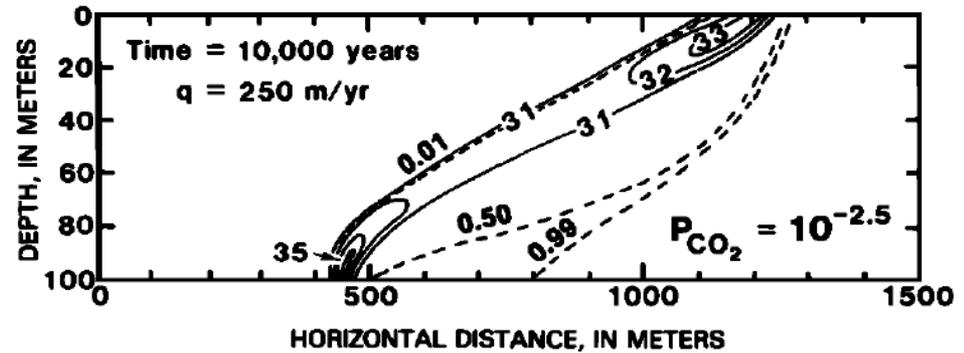
Chemical Reactions: karst



# Calcite Dissolution - Coastal Aquifers

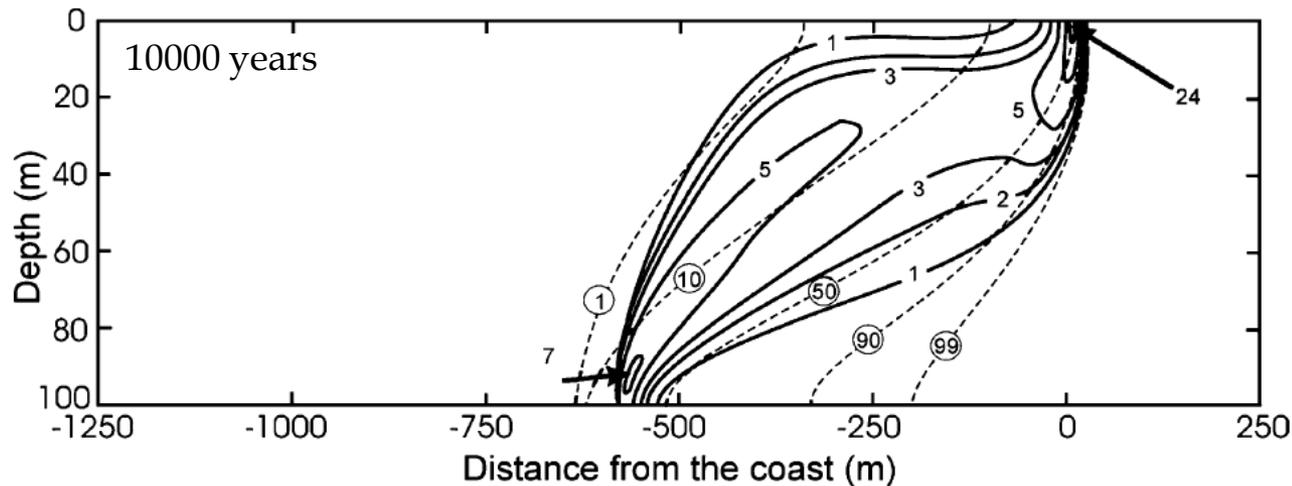


Sanford and Konikow, Water Resour. Res. (1989)



**EXPLANATION**  
 — 32 — Percent porosity  
 - - - 0.50 - - - Fraction seawater

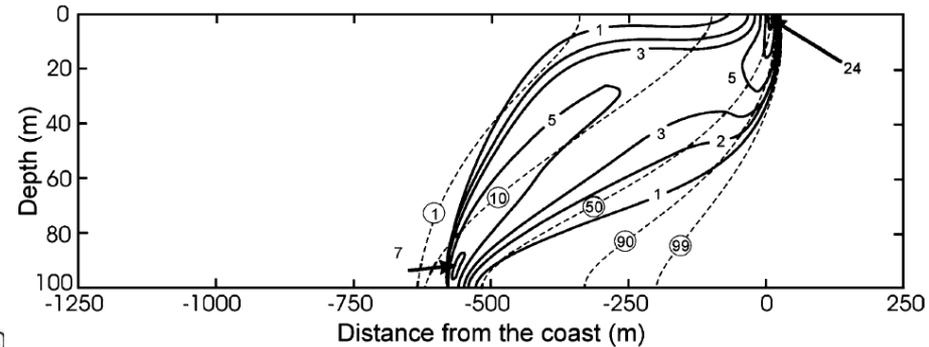
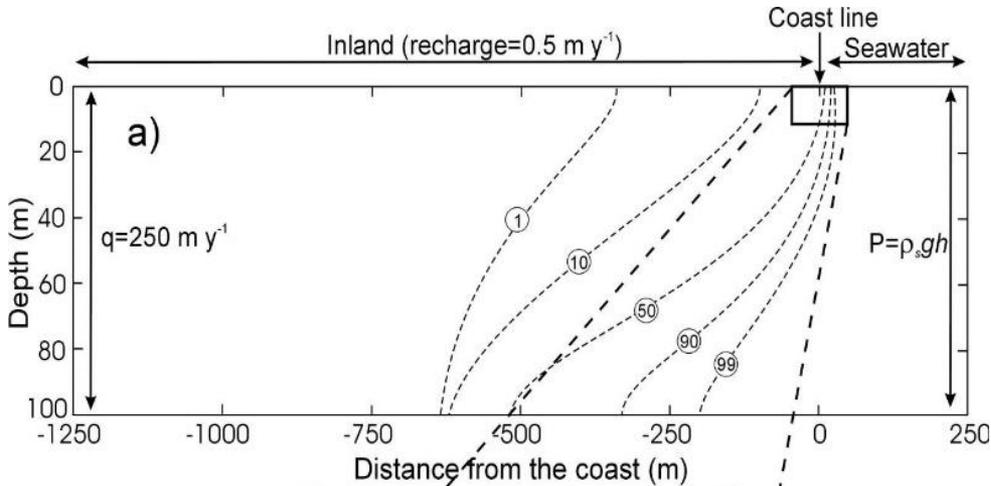
## Fully Coupled Reactive transport



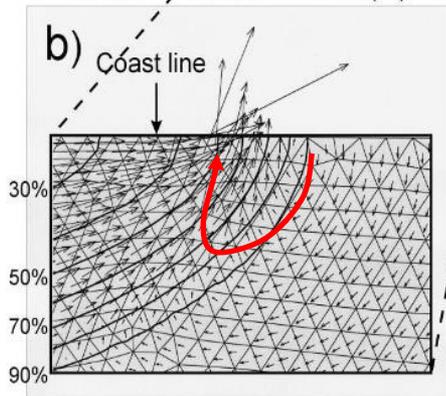
Rezaei et al, J. Hydrology, 2005

Transport processes (mixing) control how much, when, and where dissolution occurs.

# Calcite Dissolution - Coastal Aquifers



Rezaei et al, Water Resour. Reseach 2005



Dissolution tends to concentrate at the freshwater side of the mixing zone, except at the discharge area, where dissolution is maximum near the saline side.

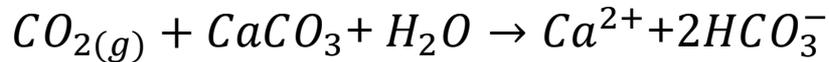
The  $\text{PCO}_2$  of both end-members control the rate of dissolution

# Calcite Dissolution - Approach

## Calcite Dissolution

We consider:

An instantaneous dissolution reaction  
(pure dissolution at equilibrium)



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

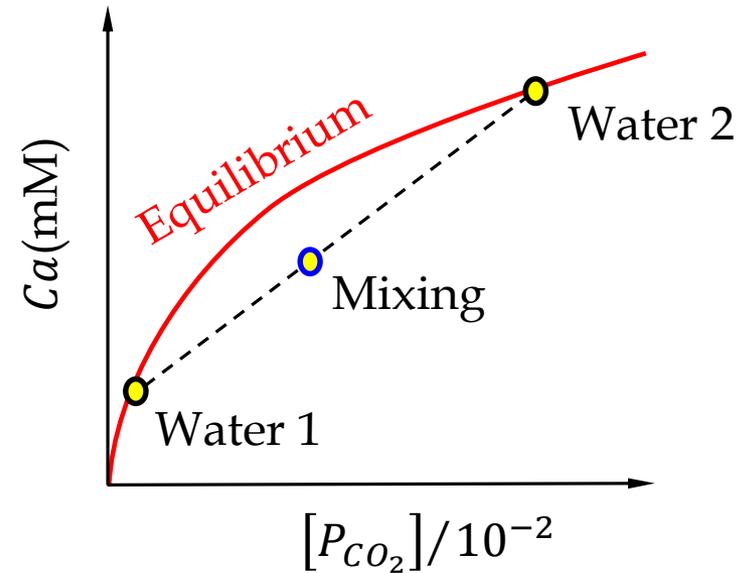
$$\frac{\partial C_2}{\partial t} - L_t(C_2) = -r \quad (2)$$

$$L_t(C) = -\mathbf{q}\nabla C + \nabla \cdot (\mathbf{D}\nabla C)$$

$$(1)-(2): \quad \frac{\partial \alpha}{\partial t} = L_t(\alpha)$$

Conservative Component

$$\alpha = C_1 - C_2$$



Appelo & Postma, Geochemistry, groundwater and pollution

# Calcite Dissolution - Approach

Calcite Dissolution

$$\frac{\partial \alpha}{\partial t} = L_t(\alpha)$$

$$L_t(C) = -\mathbf{q}\nabla C + \nabla \cdot (\mathbf{D}\nabla C)$$

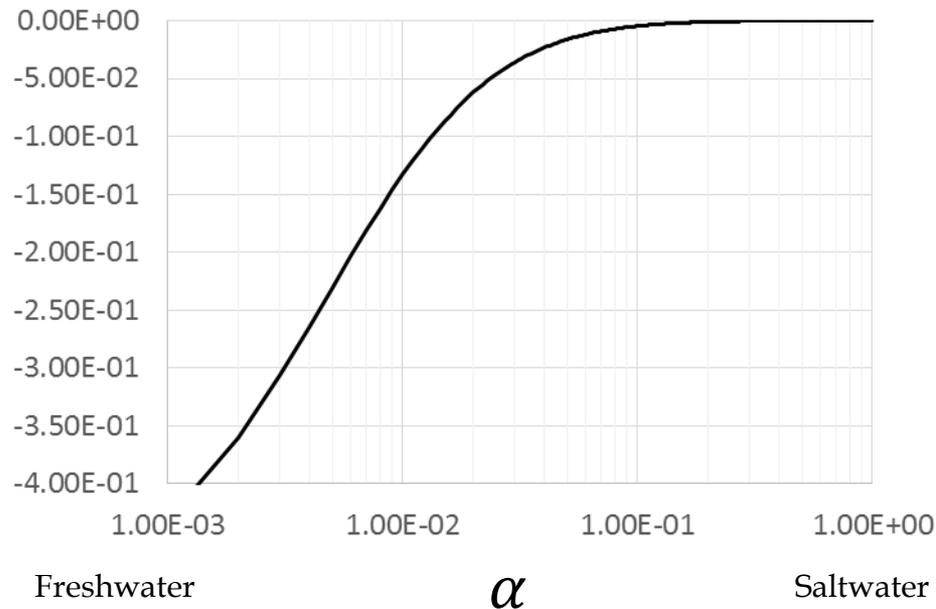
Reaction Rate

$$r = \frac{\partial^2 C_2}{\partial \alpha^2} (\nabla^T \alpha \mathbf{D} \nabla \alpha)$$

Numerical Model  
(conservative)

Phreeqc

$$\frac{\partial^2 C_{Ca^{2+}}}{\partial \alpha^2}$$



# Calcite Dissolution - Approach

## Calcite Dissolution

Reaction Rate

$$r = \frac{\partial^2 C_2}{\partial \alpha^2} (\nabla^T \alpha \mathbf{D} \nabla \alpha)$$

Porosity

$$\phi(t + \Delta t) = \phi(t) + r V_m \Delta t$$

Molar Volume

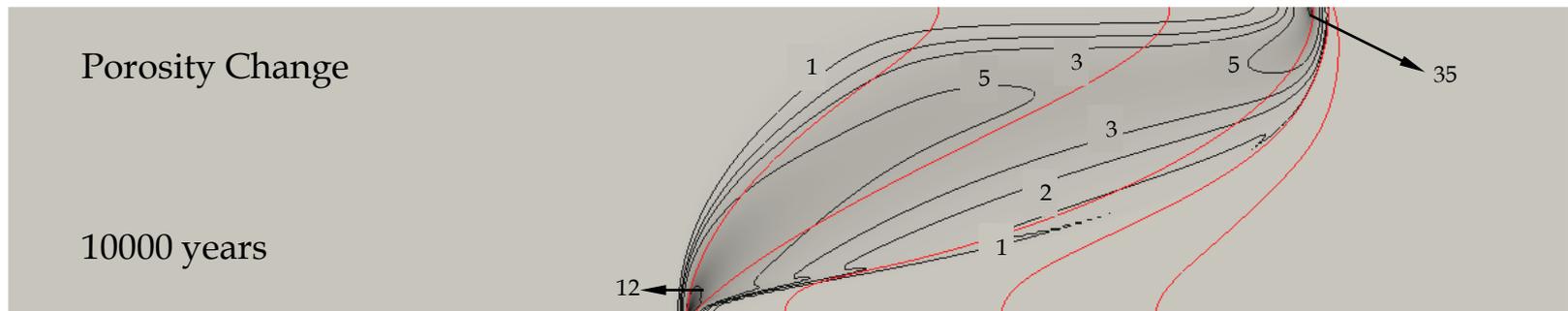
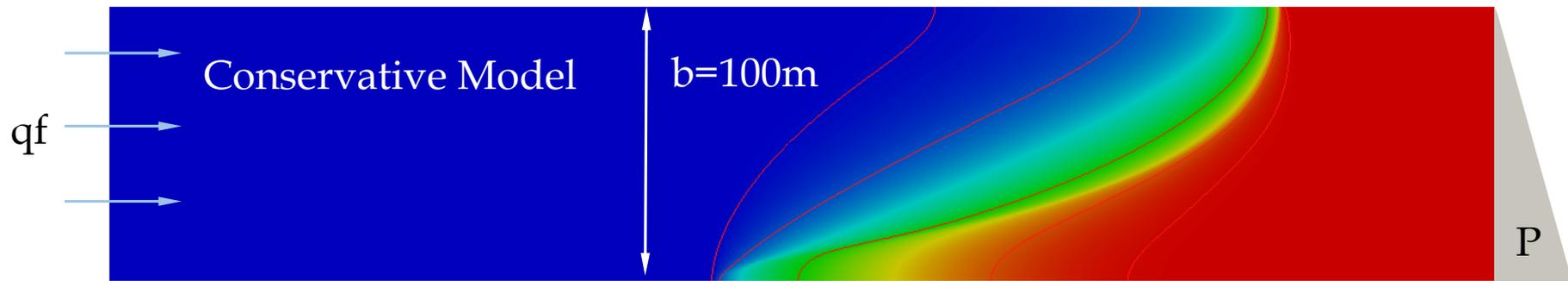
# Calcite Dissolution - Coastal Aquifers

Application

De Simoni (2005) formulation

Reaction Rate  $r = \frac{\partial^2 C_2}{\partial \alpha^2} (\nabla^T \alpha \mathbf{D} \nabla \alpha)$

Porosity  $\phi(t + \Delta t) = \phi(t) + r V_m \Delta t$



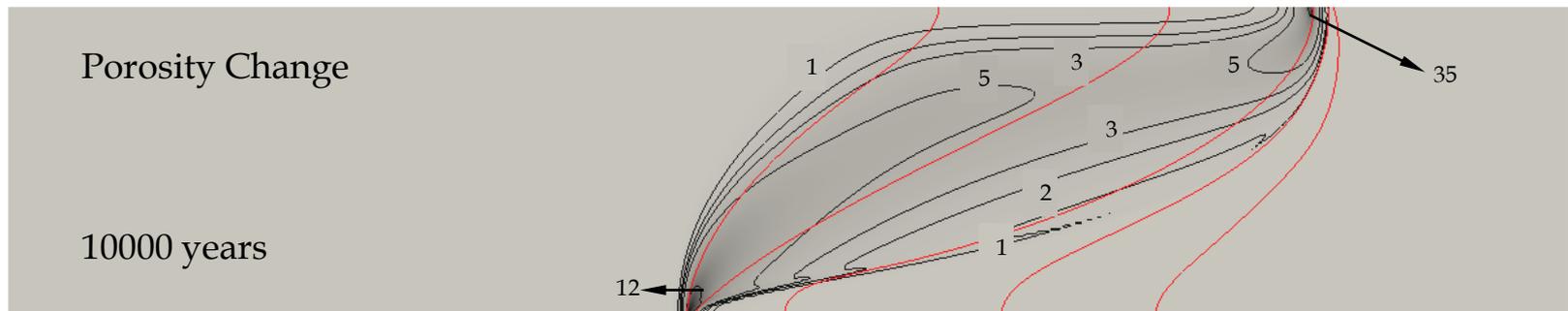
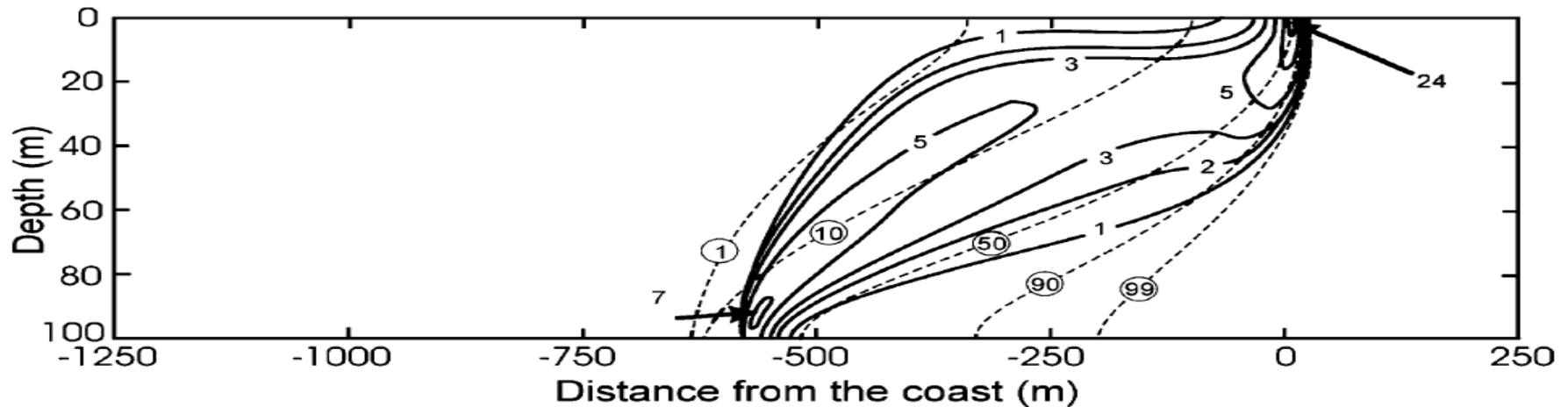
# Calcite Dissolution - Coastal Aquifers

Application

De Simoni (2005) formulation

$$\text{Reaction Rate } r = \frac{\partial^2 C_2}{\partial \alpha^2} (\nabla^T \alpha \mathbf{D} \nabla \alpha)$$

$$\text{Porosity } \phi(t + \Delta t) = \phi(t) + r V_m \Delta t$$



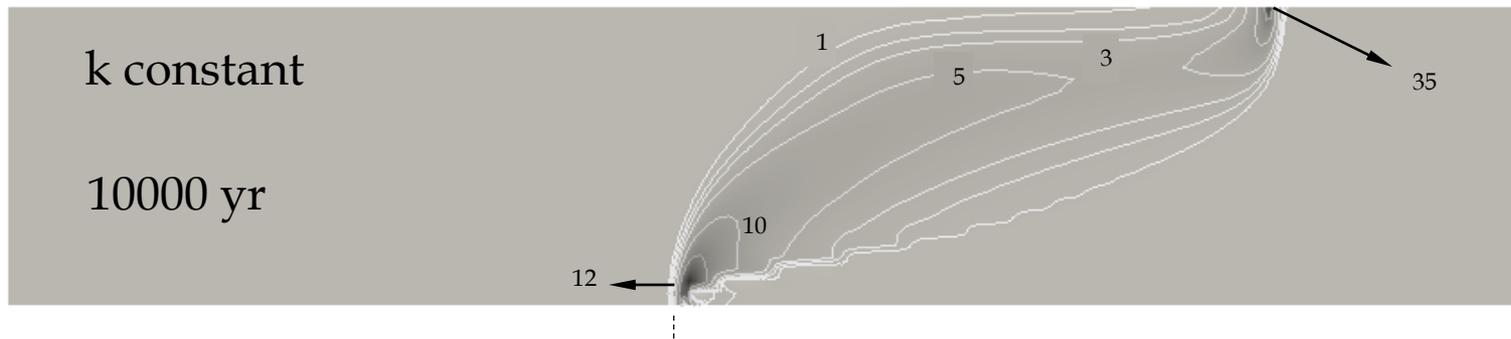
It works!!!

# Calcite Dissolution - Coastal Aquifers

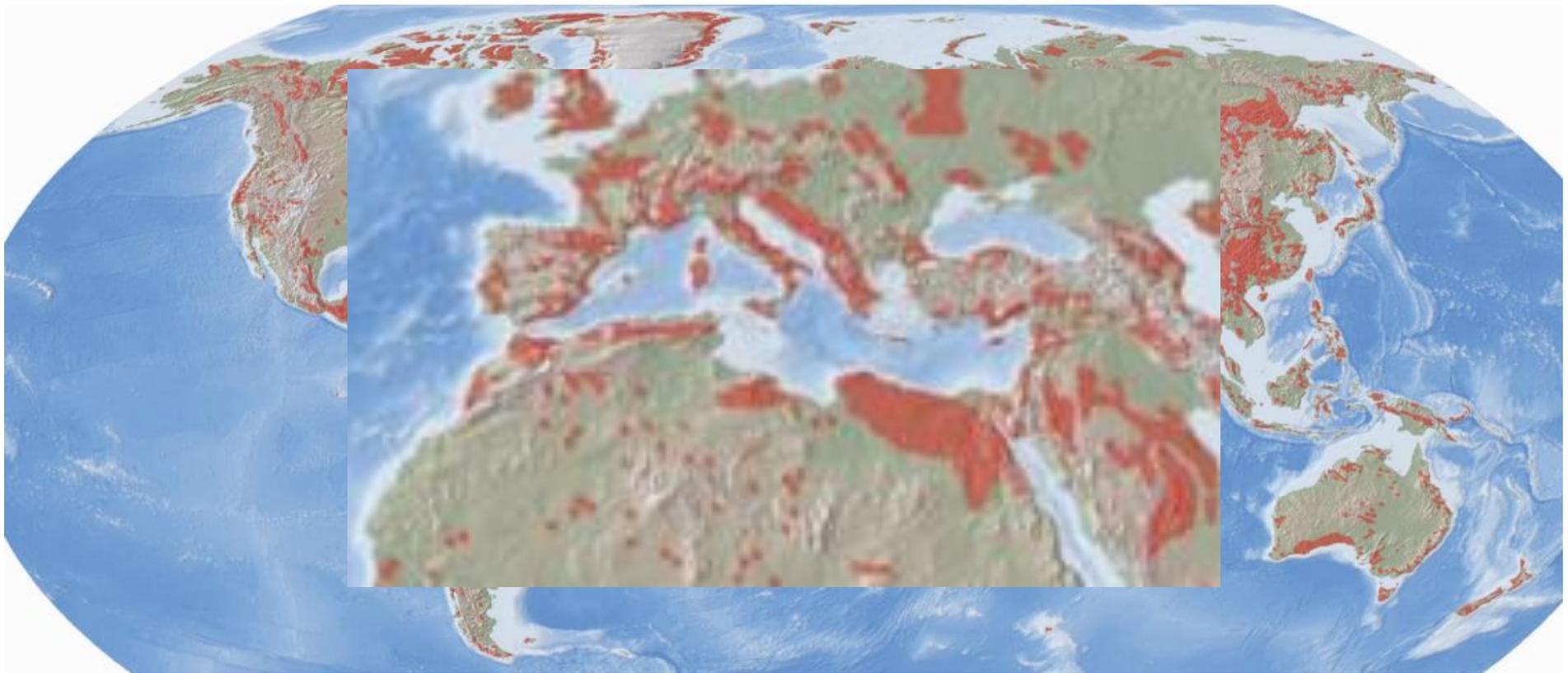
Change in Permeability

$$k(t) = k_0[\phi(t)/\phi_0]^3$$

Civan (2001), Carroll et al. (2013)

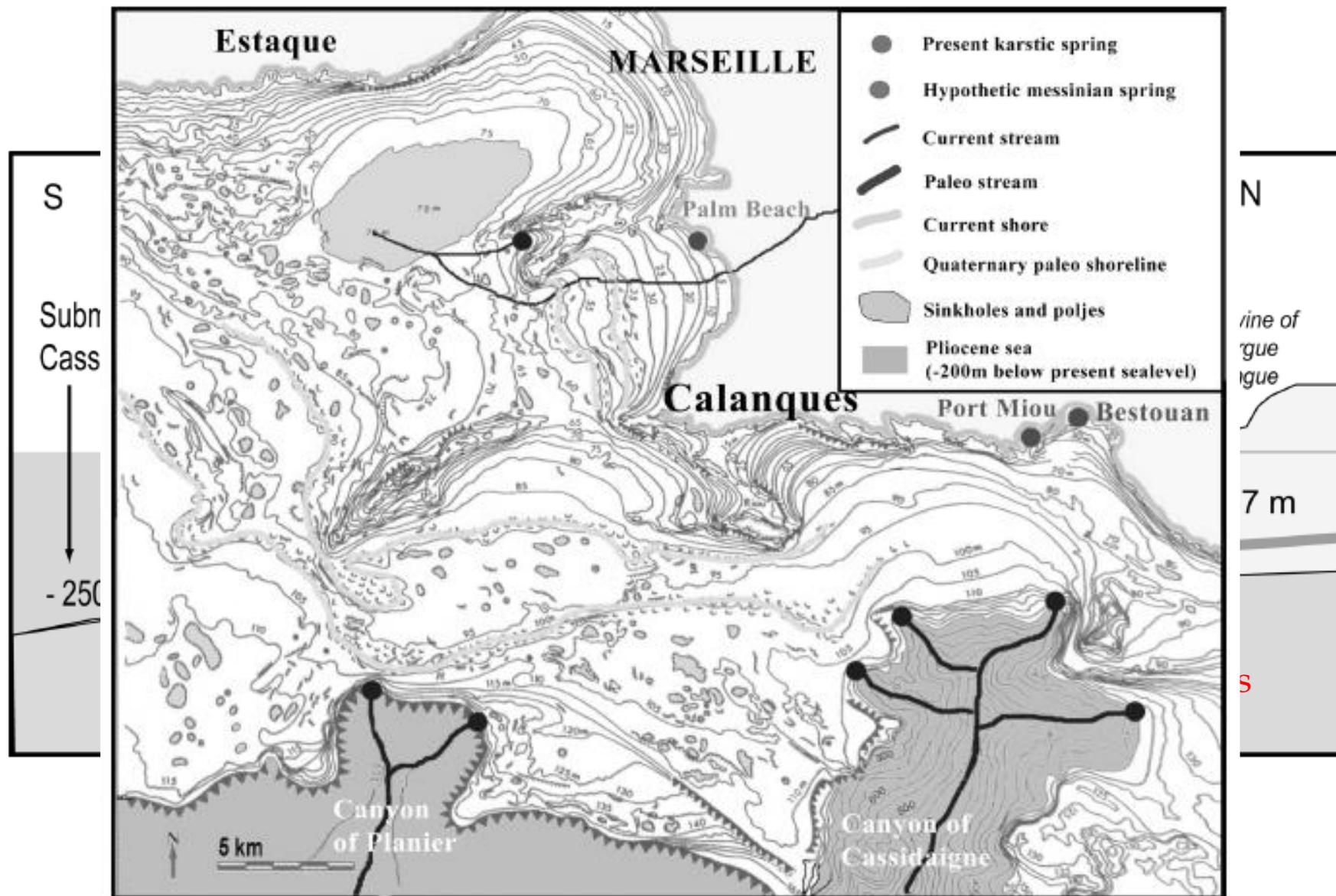


# Karst Distribution



Ford, D.C., and Williams, P.W., *Karst Geomorphology and Hydrology*,  
(1989)

# Karst Distribution



# Karst Distribution



# Hypothesis

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Karst development in response to mixing and sea level fluctuations.

# Messinian Crisis (5.96 to 5.33 million years ago)

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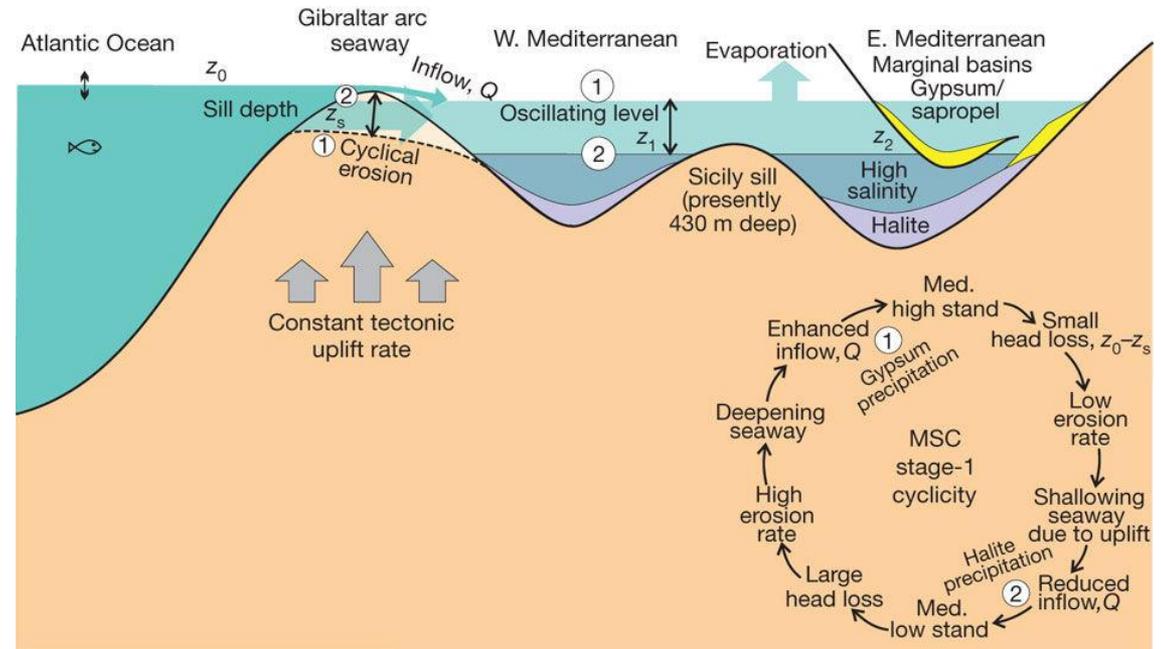
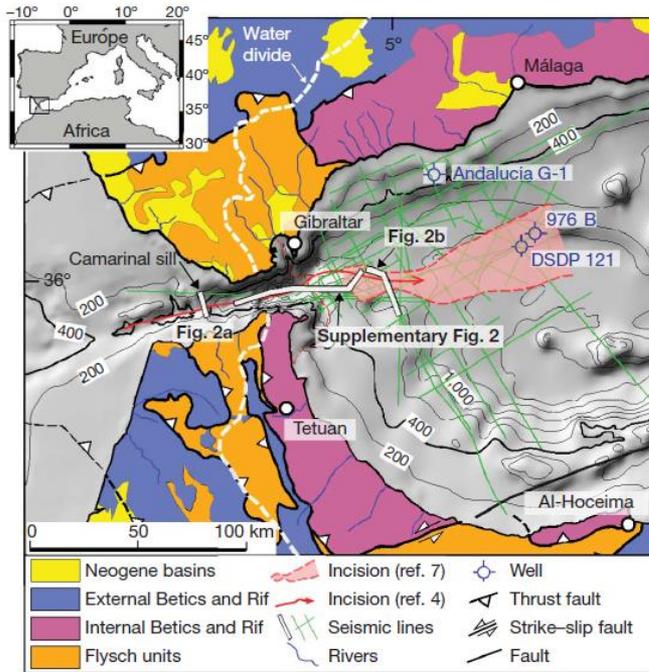
Story....Once upon a time

# Messinian Crisis (5.96 to 5.33 million years ago)

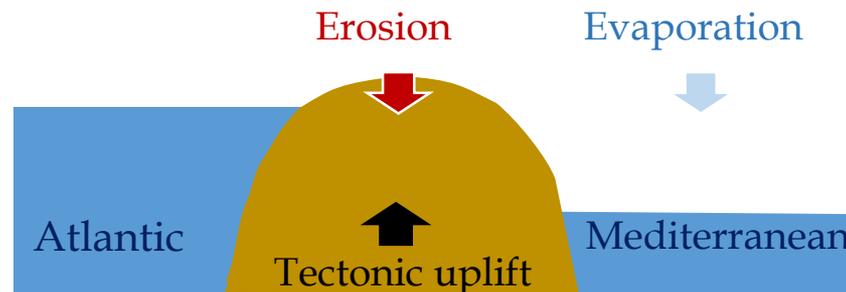
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# Messinian Crisis (5.96 to 5.33 million years ago)

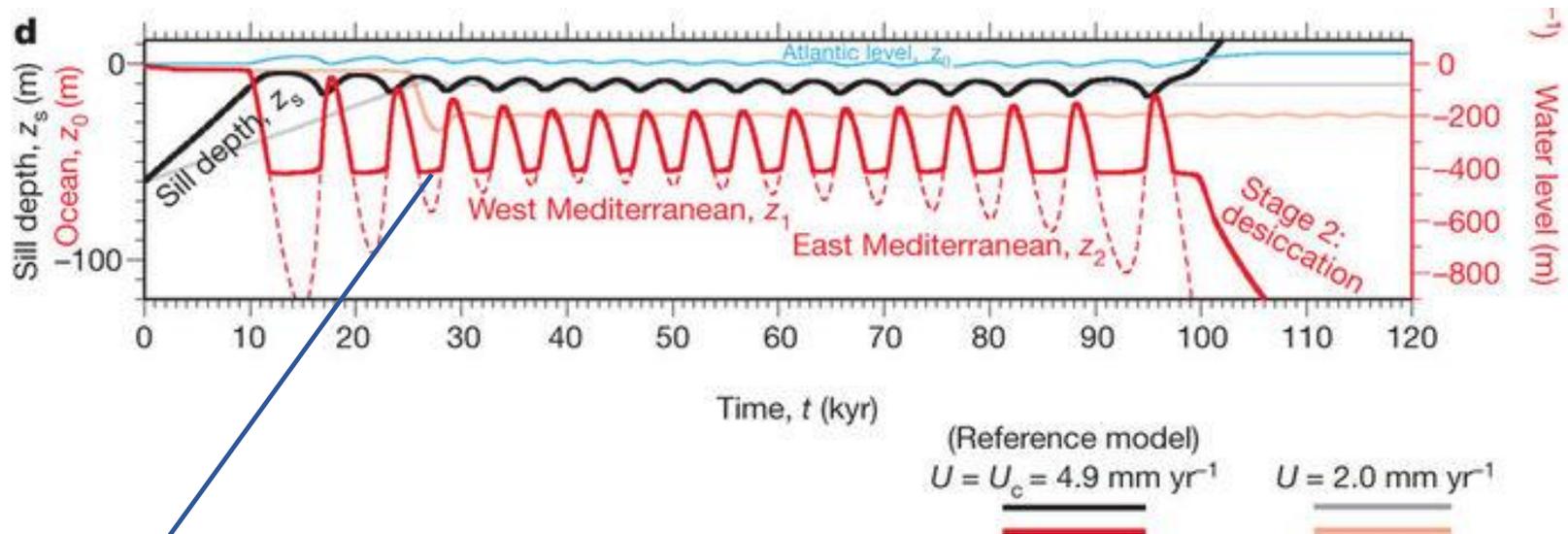


García-Castellanos et al, *Nature* (2009,2011)



# Messinian Crisis (5.96 to 5.33 million years ago)

Oscillations in sea level as the result of dynamic harmonic coupling between the drawdown and the refill triggered when erosion deepens the seaway.

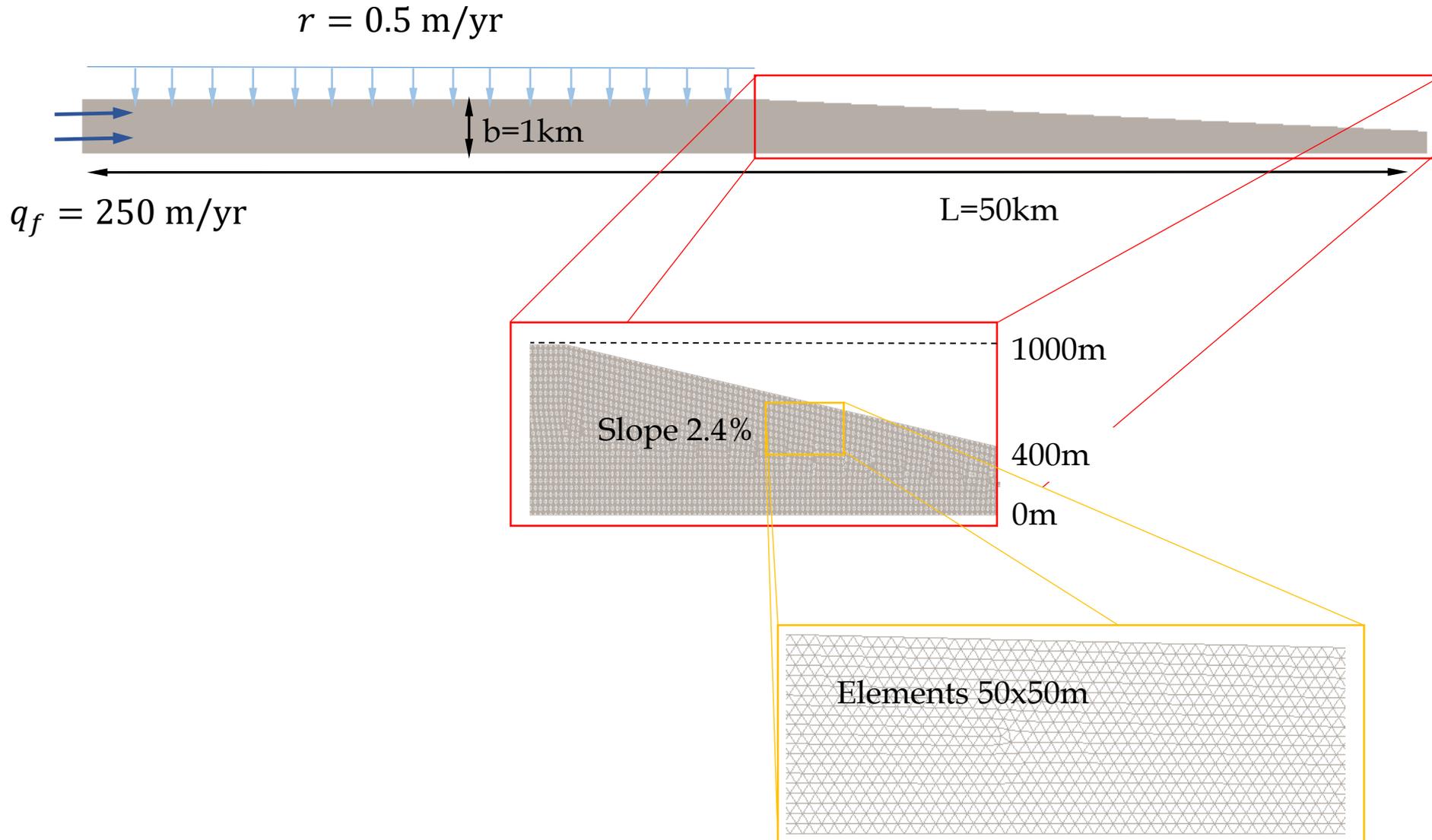


García-Castellanos et al, *Nature*, 2011

- Fluctuations of Amplitude 200m and period 6000yr

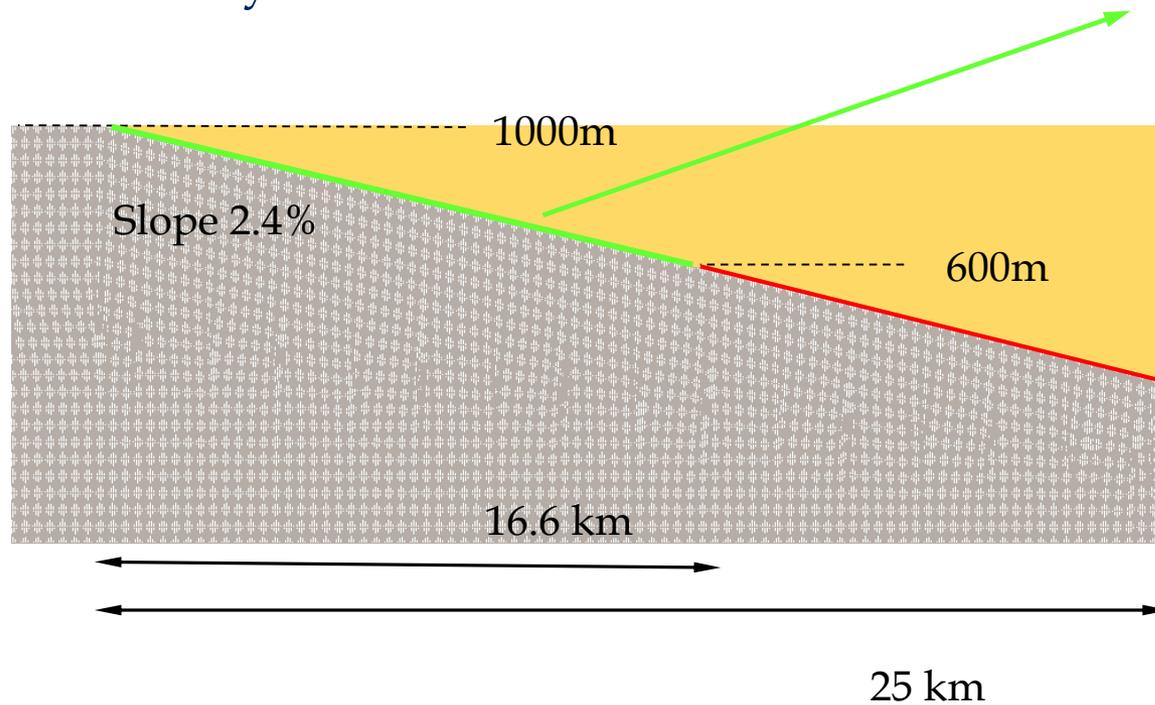
# Messinian: Conceptual Model

## Boundary Conditions I



# Messinian: Conceptual Model

## Boundary Conditions II



## Conditional Boundary Condition

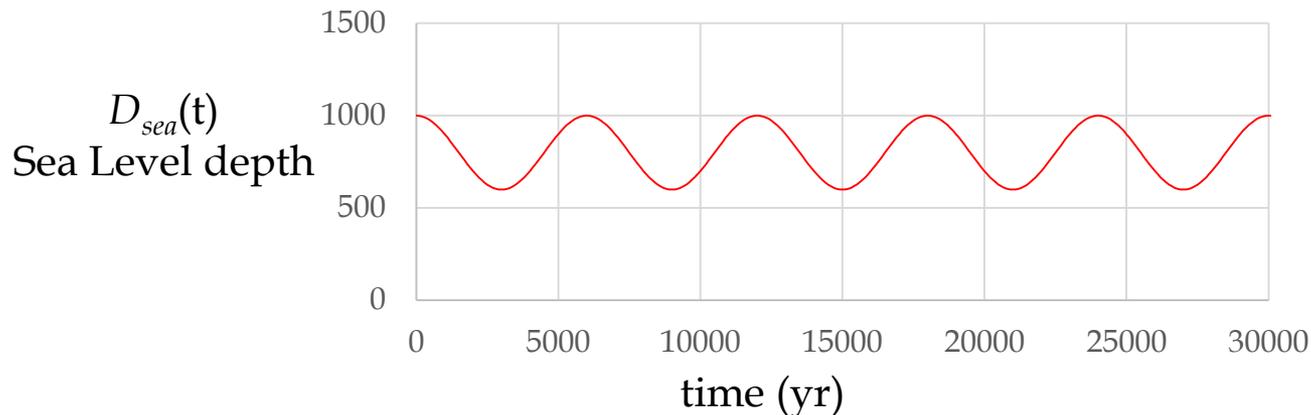
- If  $z_i < D_{sea}(t)$

$$P(t) = \rho_s g [D_{sea}(t) - z_i]$$

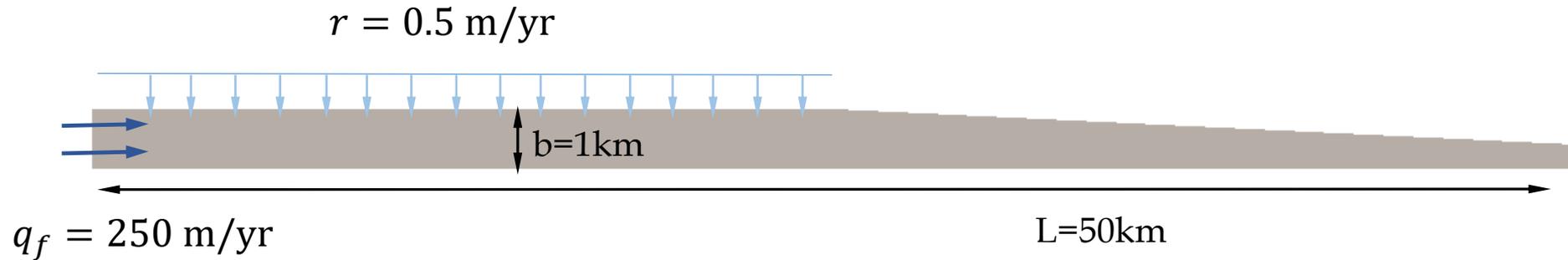
- If  $z_i > D_{sea}(t)$

$$P(t) = p$$

$$P(t) = \rho_s g [D_{sea}(t) - z_i]$$



# Messinian: Conceptual Model



De Simoni (2005) formulation

Reaction Rate 
$$r = \frac{\partial^2 C_2}{\partial \alpha^2} (\nabla^T \alpha \mathbf{D} \nabla \alpha)$$

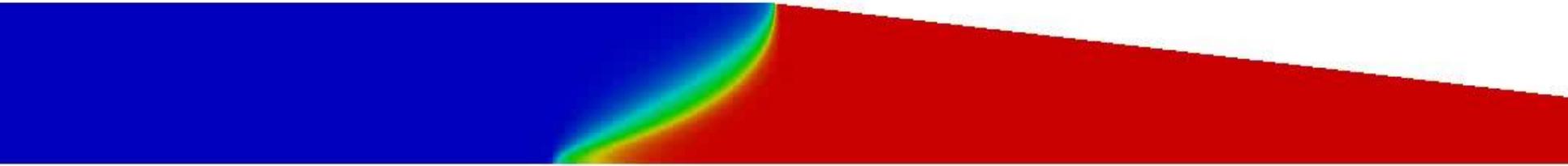
Change in Porosity 
$$\phi(t + \Delta t) = \phi(t) + r V_m \Delta t$$

Change in Permeability 
$$k(t) = k_0 [\phi(t) / \phi_0]^3$$

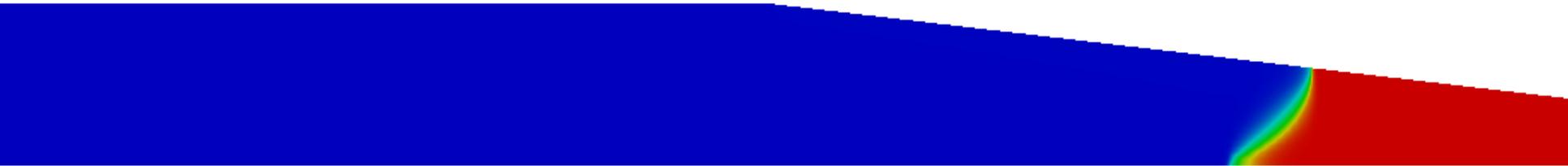
# Messinian: Results

---

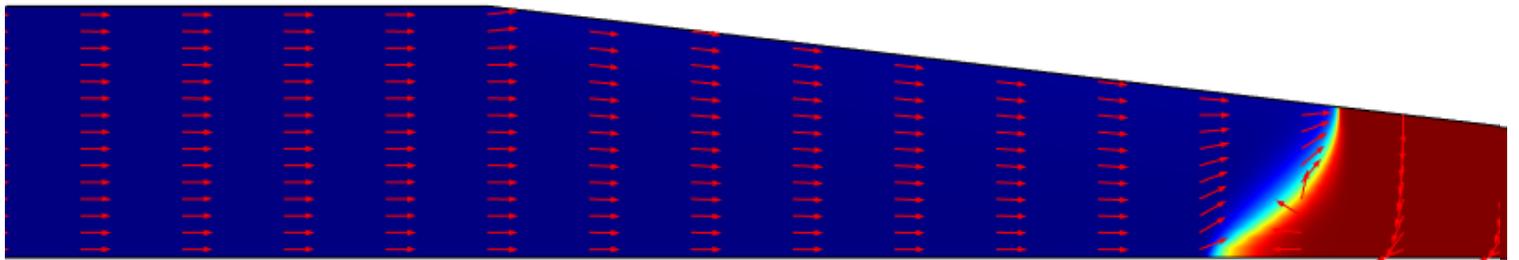
Concentration distribution (6000 yr, 1 cycle)



# Messinian: Results



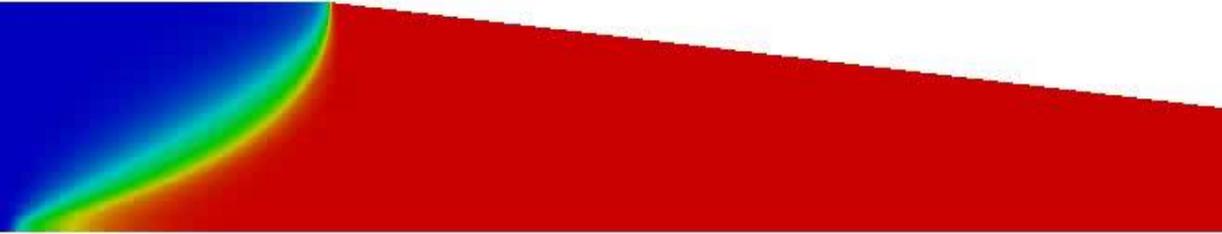
Seaward



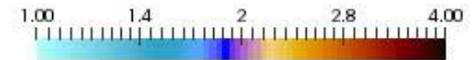
# Messinian: Results

24000 yr, 4 cycles

Concentration distribution  
Change in porosity (%)



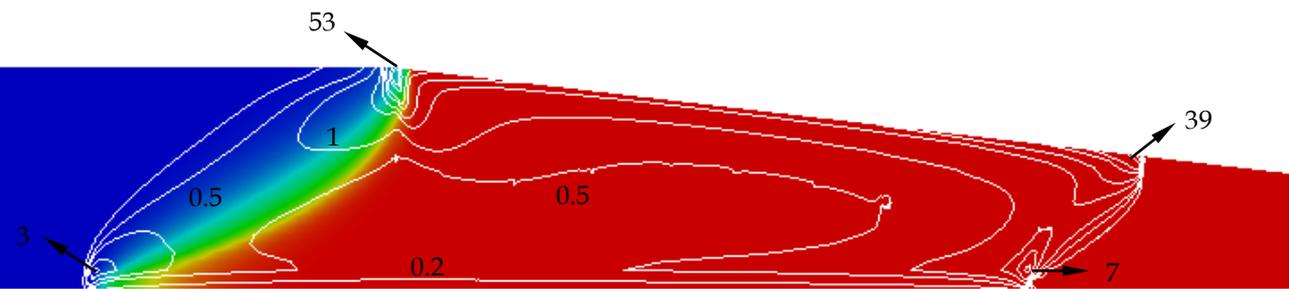
Change in permeability(%)



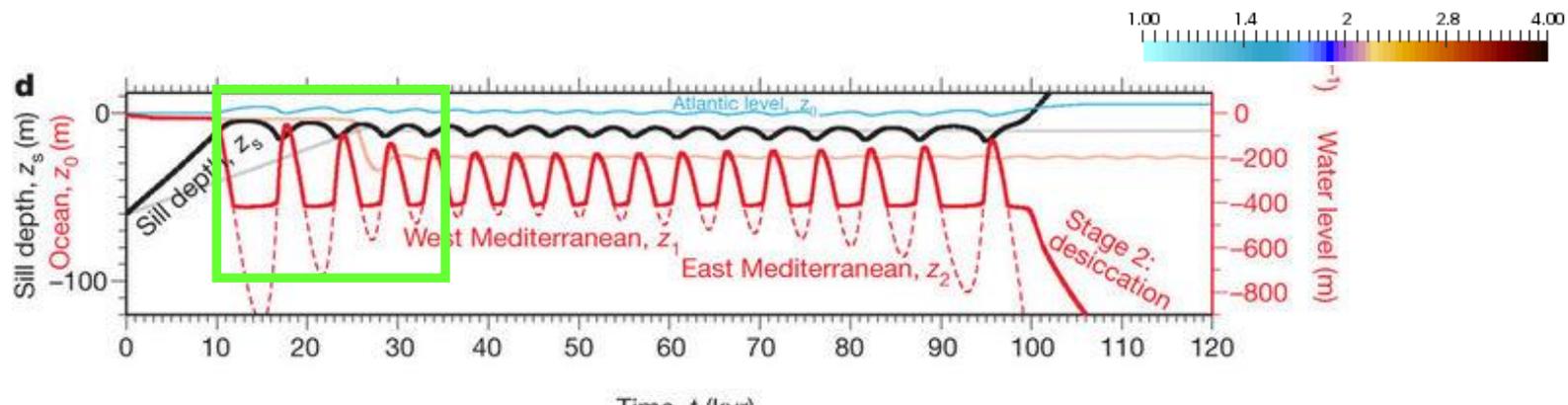
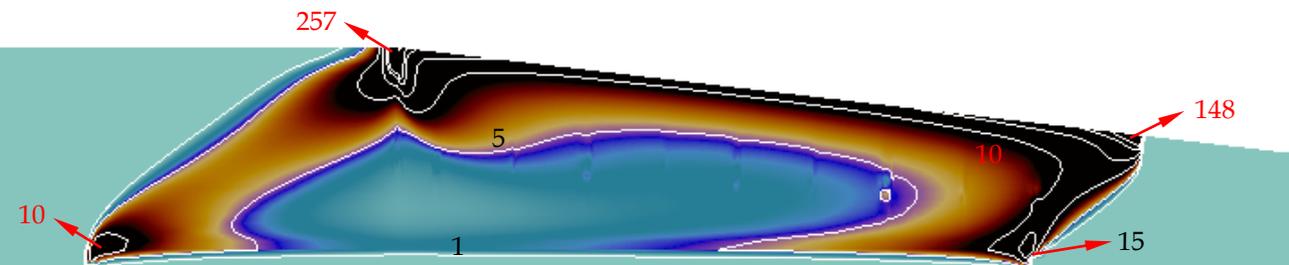
# Messinian: Results

24000 yr, 4 cycles

Concentration distribution  
Change in porosity (%)

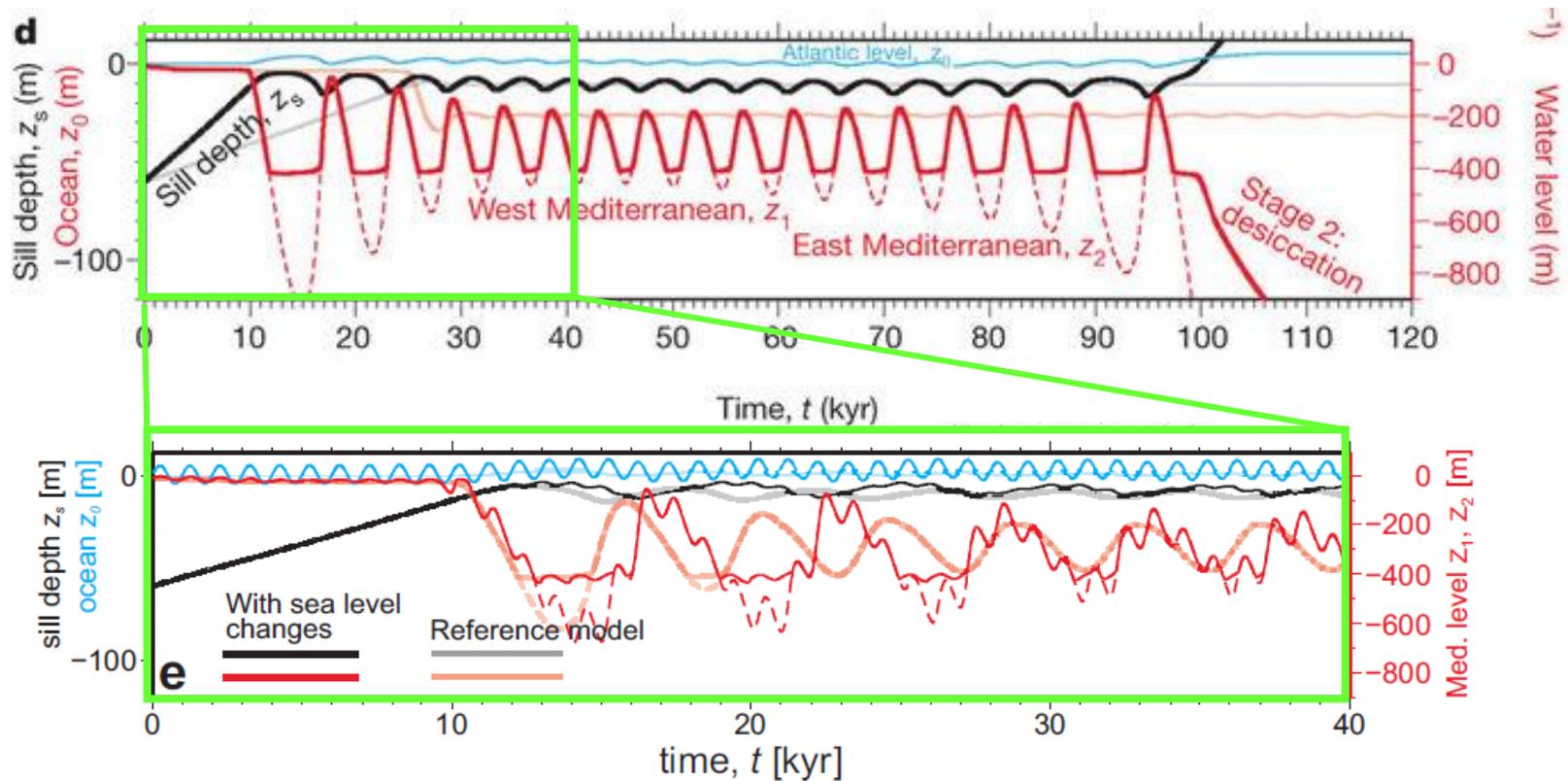


Change in permeability (%)



# Messinian Crisis (5.96 to 5.33 million years ago)

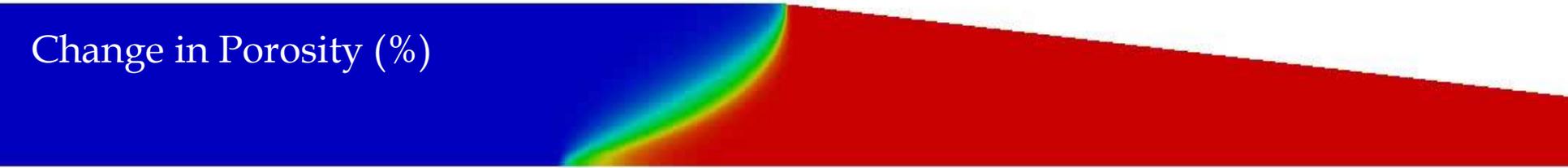
More complex temporal fluctuations  
Including changes in the Atlantic Level



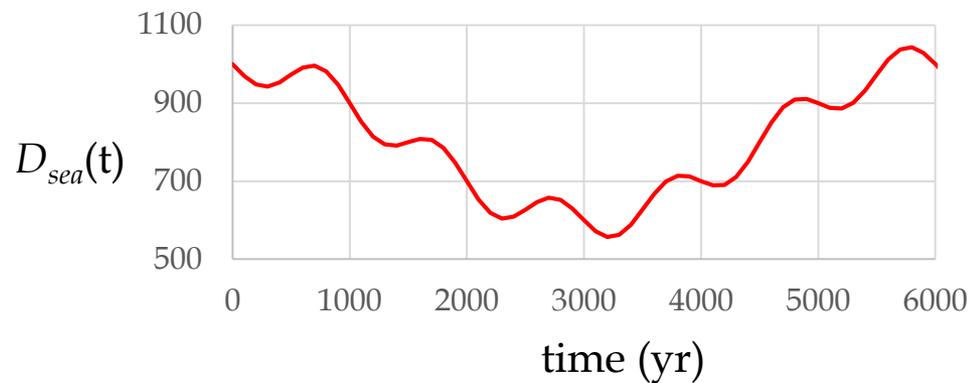
# Messinian: Results

6000 yr (1 cycle)

Change in Porosity (%)

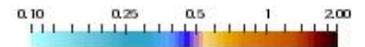
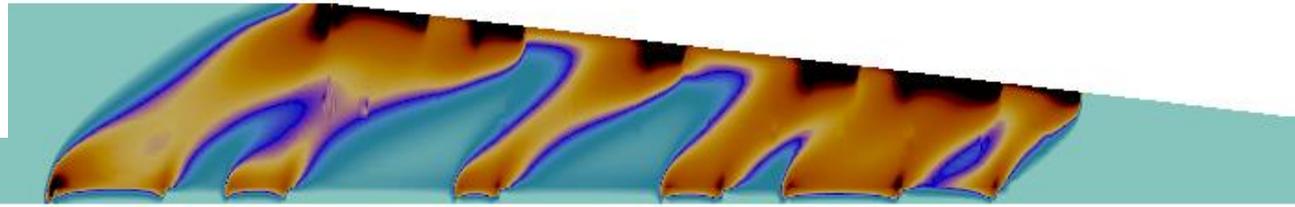
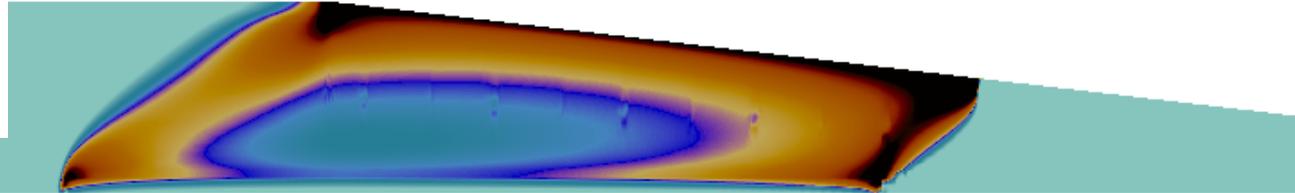


Change in Permeability (%)



# Messinian: Results

6000 yr (1 cycle)



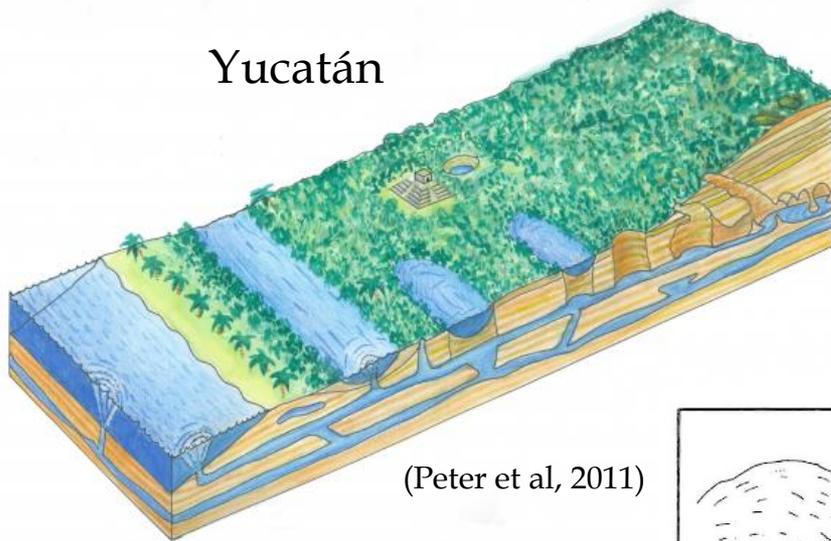
# Conclusions

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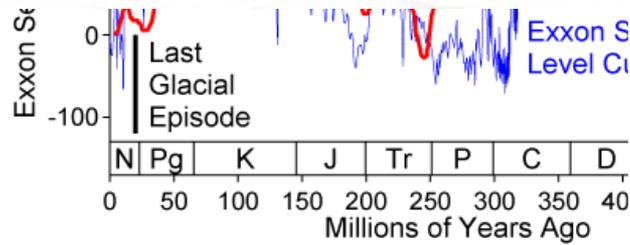
- The coupling of temporal fluctuations and density-driven flow can be a **very likely mechanism** for the formation of geochemical reaction patterns observed in coastal **karst aquifers**.

# Not only in the Mediterranean

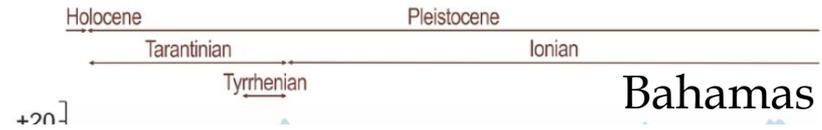
Yucatán



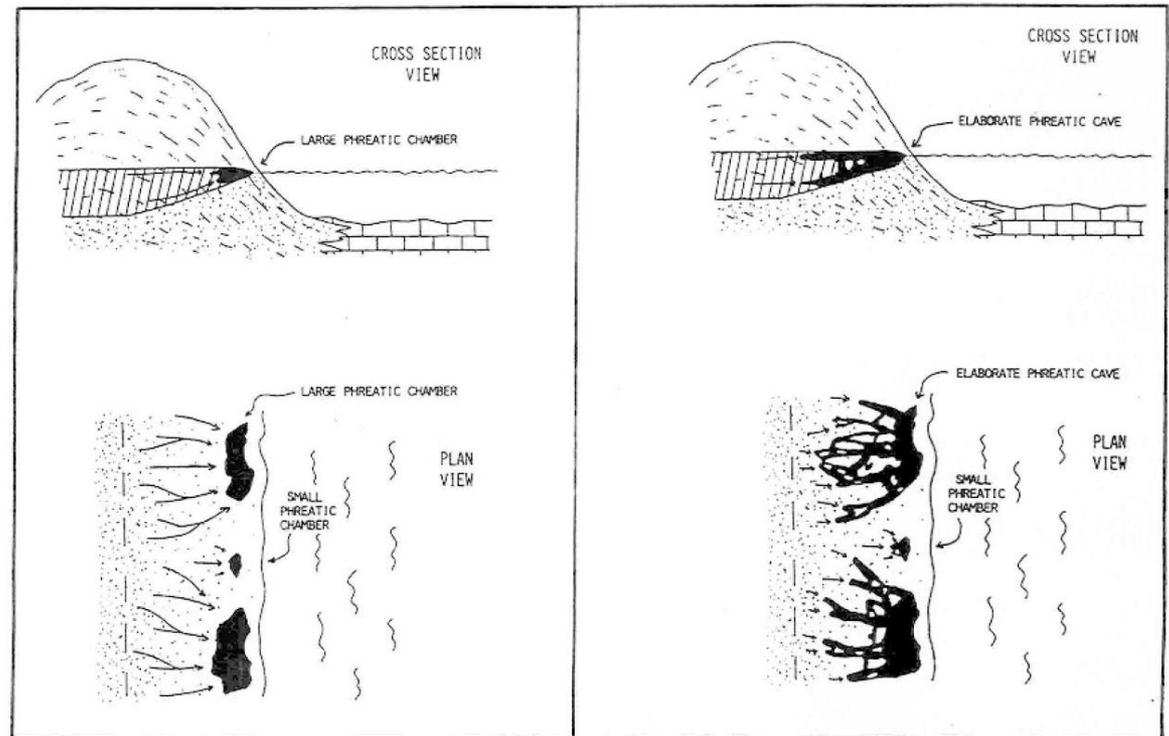
(Peter et al, 2011)



Hallan



Bahamas



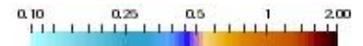
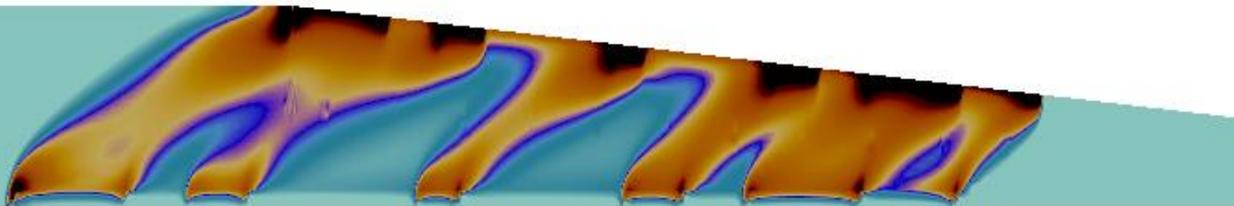
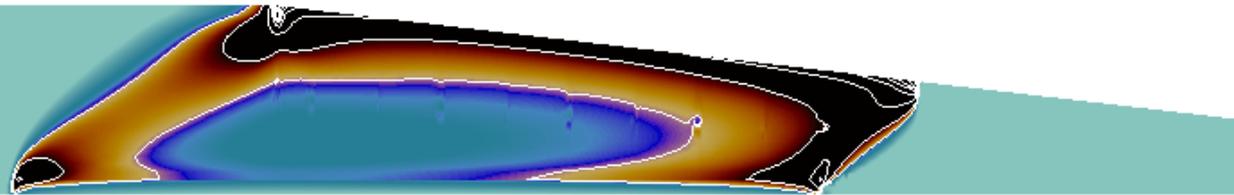
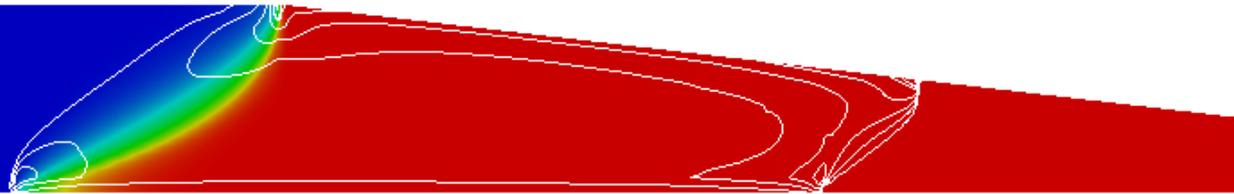
Myroie et al. 1990

# Conclusions

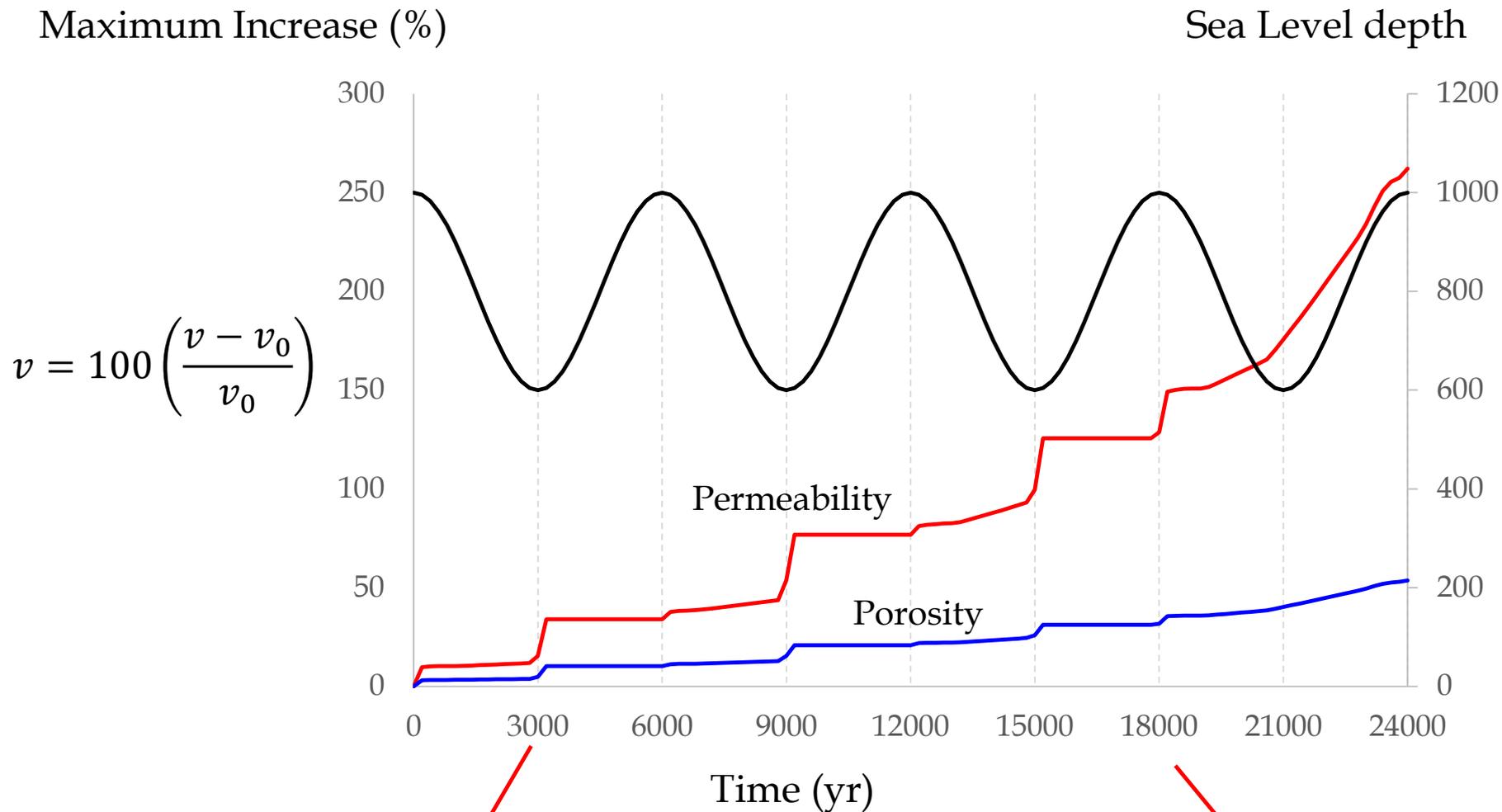
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- The coupling of temporal fluctuations and density-driven flow can be a **very likely mechanism** for the formation of geochemical reaction patterns observed in coastal **karst aquifers**.
- Long period fluctuations promote horizontal conduit networks and irregular and short period fluctuations promote sinkholes and vertical karst conduits.

# Thanks

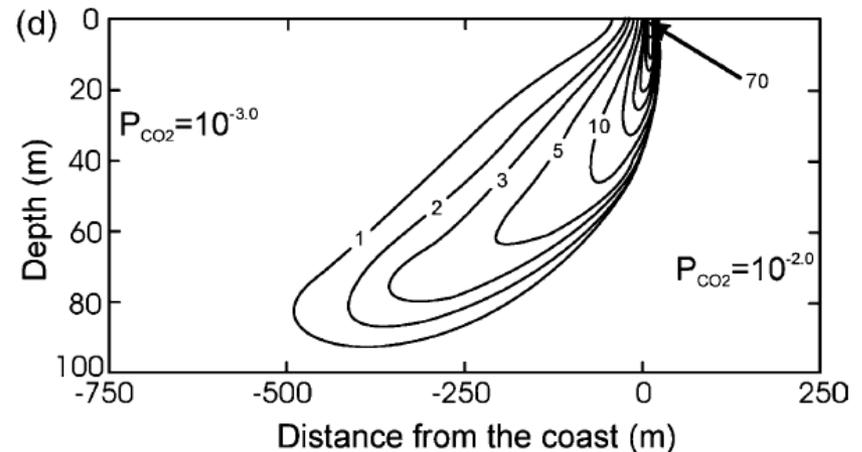
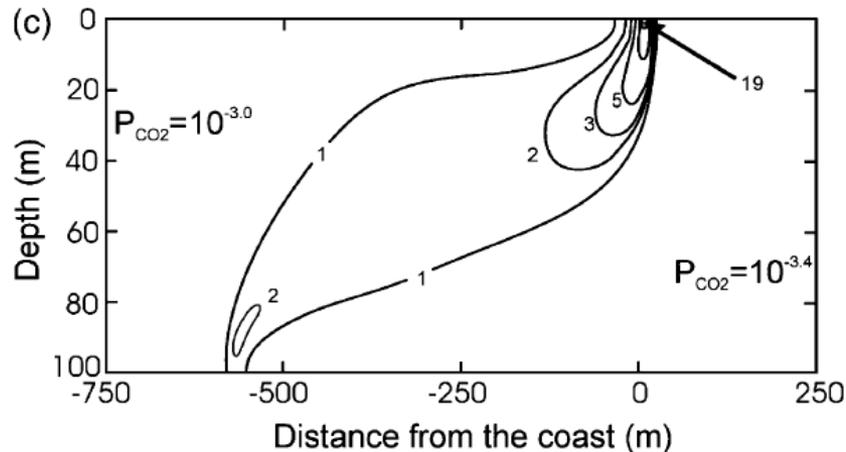
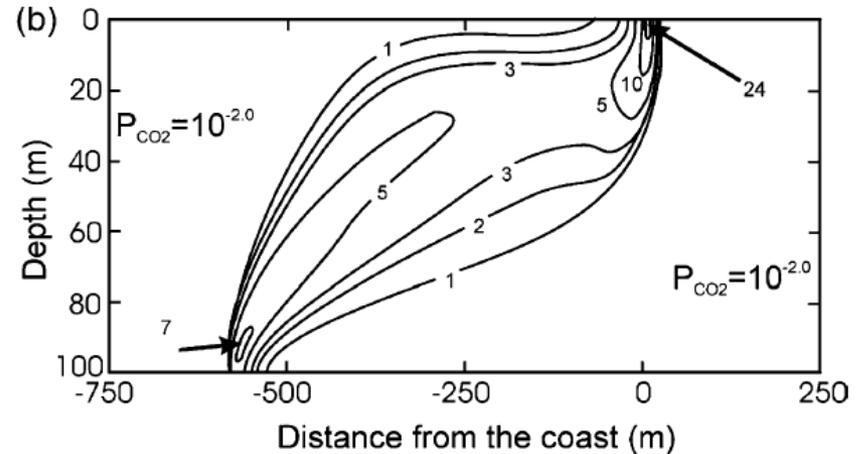
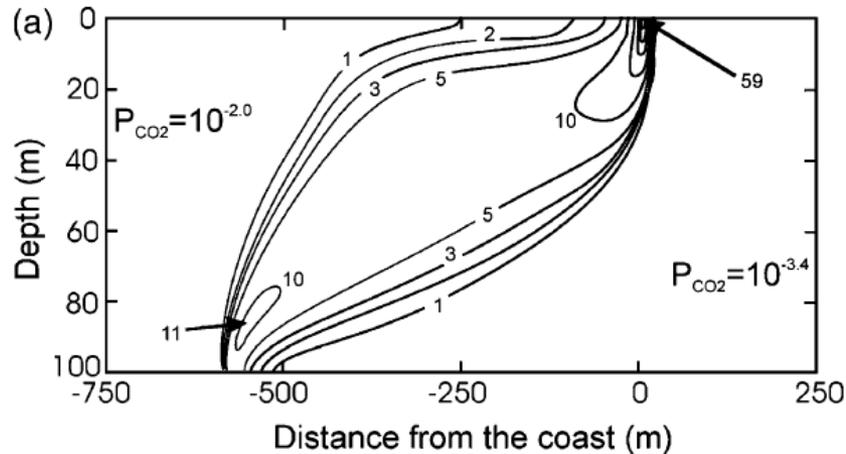


# Messinian: Results



# Calcite Dissolution - Coastal Aquifers

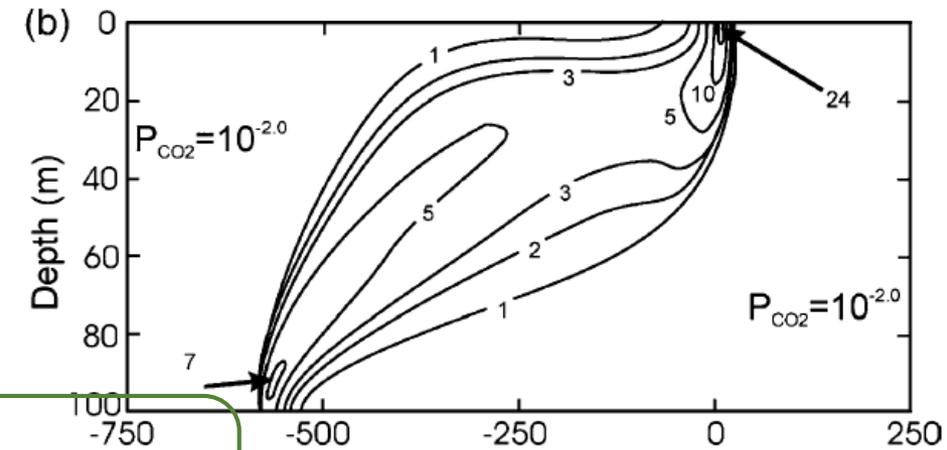
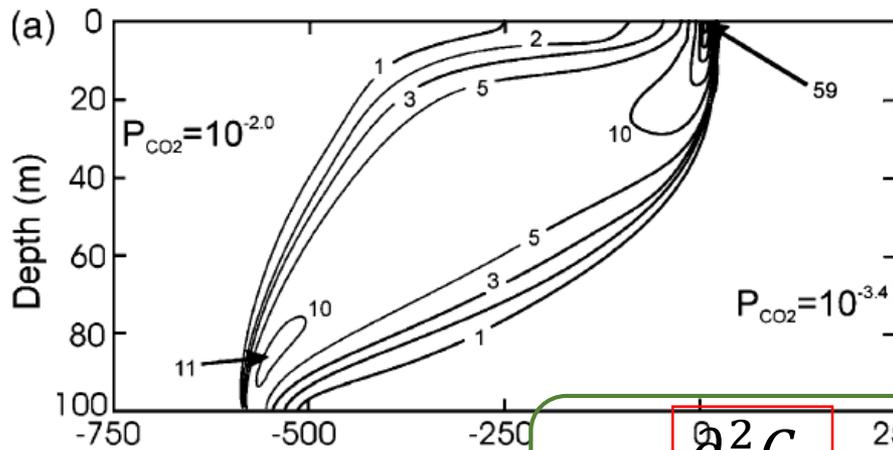
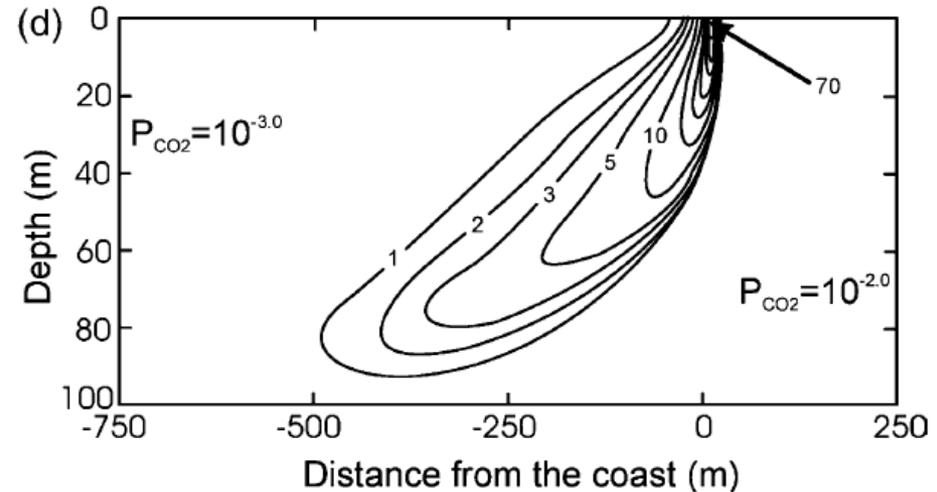
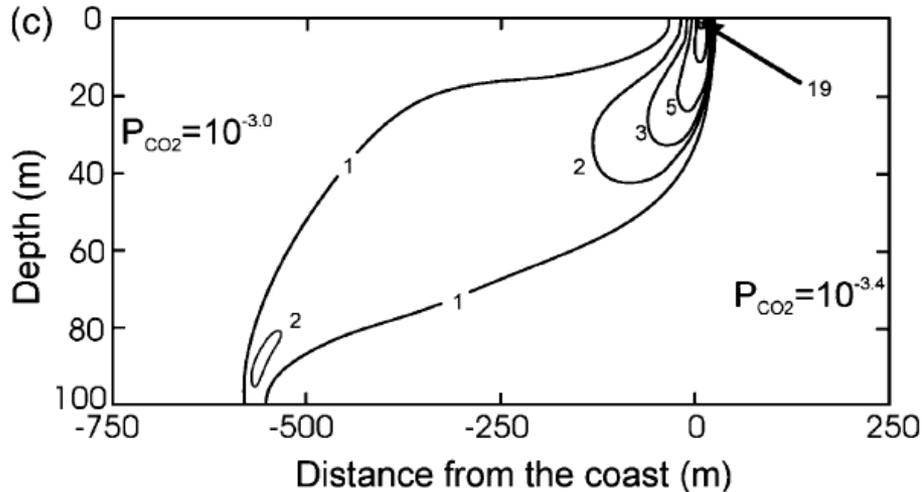
The  $P_{CO_2}$  of both end-members control the rate of dissolution



- The larger  $P_{CO_2}$  the more reactive
- Differences in  $P_{CO_2}$  between the endmember solutions results in an increase of total accumulated calcite dissolution

# Calcite Dissolution - Coastal Aquifers

The  $P_{CO_2}$  of both end-members control the rate of dissolution



Reaction Rate

$$r = \frac{\partial^2 C_2}{\partial \alpha^2} (\nabla^T \alpha \mathbf{D} \nabla \alpha)$$

# Messinian Crisis (5.96 to 5.33 million years ago)

