

# **PS Basin Modelling and Diagenetic Effects of Groundwater Migration\***

**Xavier Guichet<sup>1</sup> and Sylvie Wolf<sup>2</sup>**

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<sup>1</sup>Geology-Geochemistry-Geophysics, IFP, Rueil-Malmaison, France ([xavier.guichet@ifp.fr](mailto:xavier.guichet@ifp.fr))

<sup>2</sup>Applied Mathematics, IFP, Rueil-Malmaison, France

## **Abstract**

Our objective is to trace the volume of minerals that precipitate or dissolve in a sedimentary basin as groundwaters migrate along temperature and pressure gradients. In a sedimentary basin, temperature and pressure changes can occur in response to burial and exhumation or changes in heat flow. On the other hand, in a steady-state flow regime (T and P do not change with time), cementation only results from hydrologic mass transport. Our calculation is based on the assumption that minerals maintain local equilibrium with migrating groundwaters and their solubilities depend only on temperature and pressure. Thus every temperature and pressure change known by groundwater leads to a precipitation or a dissolution of the mineral in order to preserve local equilibrium. We developed a prototype based on Temis3D® Software, which is a coupled numerical simulation program that evaluates pore pressure, porosity, overburden and other petroleum parameters through time. Our prototype uses built-in solubility correlations to calculate solubilities of a large collection of minerals as a function of temperature and pressure. Finally the cementation or dissolution rate of a mineral is calculated in each cell of the basin model by solving a mass balance equation that describes transport of the dissolved mineral by advection. The prototype predicts cumulative volume changes of minerals following instantaneous rates of precipitation and dissolution and highlights area where cementation processes are expected to occur. Since our model does not take into account more complex geochemical factors that might control mineral precipitation or dissolution such as reaction kinetics or mixing fluids of differing composition, quantitative estimate of volume changes of minerals must be interpreted with caution.

## References

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### ABSTRACT

Our objective is to trace the volume of minerals that precipitate or dissolve in a sedimentary basin as groundwaters migrate along temperature and pressure gradients. In a sedimentary basin, temperature and pressure changes can occur in response to burial and exhumation or changes in heat flow. On the other hand, in a steady-state flow regime (T and P do not change with time), cementation only results from hydrologic mass transport. Our calculation is based on the assumption that minerals maintain local equilibrium with migrating groundwaters and their solubilities depend only on temperature and pressure. Thus every temperature and pressure change known by groundwater leads to a precipitation or a dissolution of the mineral in order to preserve local equilibrium. We developed a prototype based on Temis3D Software, which is a coupled numerical simulation program that evaluates pore pressure, porosity, overburden and other petroleum parameters through time. Our prototype uses built-in solubility correlations to calculate solubilities of a large collection of minerals as a function of temperature and pressure. Finally the cementation or dissolution rate of a mineral is calculated in each cell of the basin model by solving a mass balance equation that describes transport of the dissolved mineral by advection. The prototype predicts cumulative volume changes of minerals following instantaneous rates of precipitation and dissolution and highlights area where cementation processes are expected to occur. Since our model does not take into account more complex geochemical factors that might control mineral precipitation or dissolution such as reaction kinetics or mixing fluids of differing composition, quantitative estimate of volume changes of minerals must be interpreted with caution.

### MODEL OUTLINES

We wrote the mass balance equation for a mineral i in a volume V of the basin with a porosity  $\phi$ . Since in diagenetic problems, it is more useful to know the porosity changes following the change in a mineral's volume than its mass change, the conservation of mass becomes:

$$\frac{d\hat{Y}}{dt} = \text{div}(\phi V_i \vec{V}_w) + \frac{\partial(\phi V_i)}{\partial t} \quad \{1\}$$

with: -  $\hat{Y}$  the volume of mineral i precipitated or dissolved per unit volume of the formation

- $\hat{V}_i$  the dimensionless solubility, or the dissolved volume of mineral i per unit volume of groundwater, linked with the mineral's molal solubility.
- $\vec{V}_w$  the fluid velocity following the Darcy law.

The first term on the right hand side of the equation account for cementation by groundwater advection. The second describes the effects of temperature and pressure changes, as might occur in response to burial and exhumation or changes in heat flow, on cementation. For a volume V of a basin strata having a constant porosity, the equation becomes:

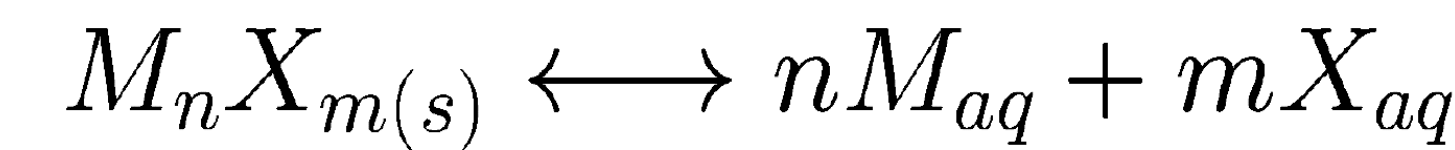
$$\frac{1}{\phi} \frac{d\hat{Y}}{dt} = \vec{V}_w \cdot \overrightarrow{\text{grad} V_i} + \frac{\partial V_i}{\partial t}$$

The last equation is equivalent to equation (13.3) of Bethke (2002).

### GEOCHEMICAL RECALL AND DATA

#### Solubility Product

The solubility product of a mineral defines the minimum product of the activities of two or more ions, that if exceeded will, under equilibrium conditions, result in the precipitation of that mineral. For a mineral  $M_n X_{m(s)}$  the reaction of dissolution/precipitation is:



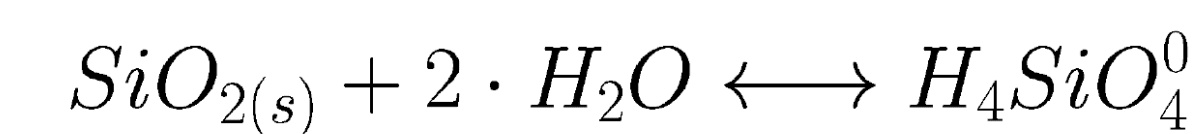
and the solubility product is:  $K_{s0} = a_{M_{aq}}^n \cdot a_{X_{aq}}^m$

with  $a_{I_{aq}}$  the activity of the aqueous species I. Solubility products are sensitive to:

-temperature / pressure / ionic strength

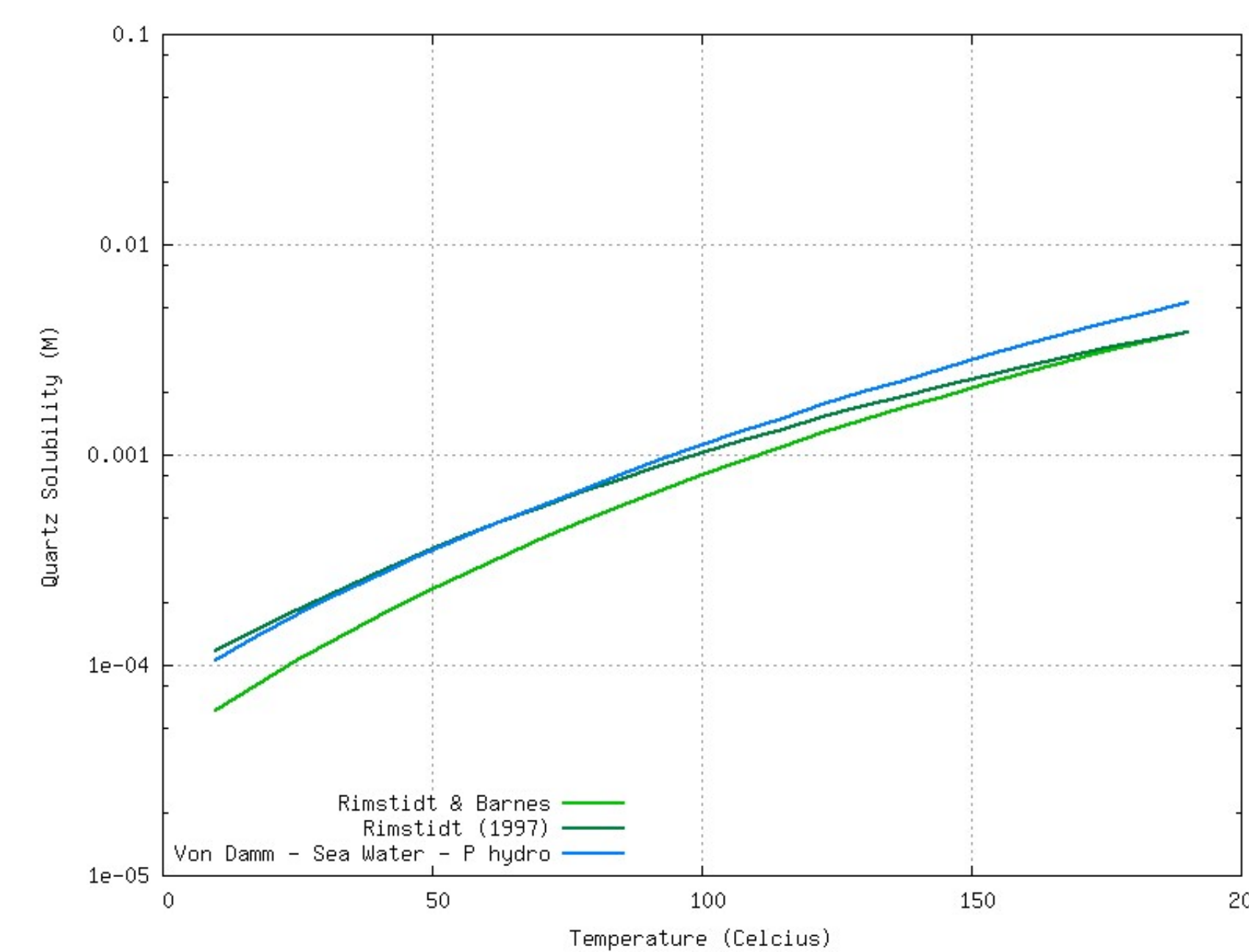
#### Apparent Solubility Product of Quartz

The chemical reaction being modeled is of the form:



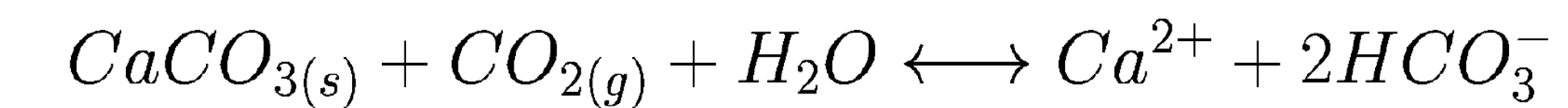
Several models for quartz solubility are available. Von Damm et al. (1991) provided a relationship calibrated for large ranges of temperature, pressure and salinity. More recently, Rimstidt (1997) gives a simple solubility function for temperature range 0-300°C:

$$\log K = -\frac{1107.12}{T} - 0.0254$$

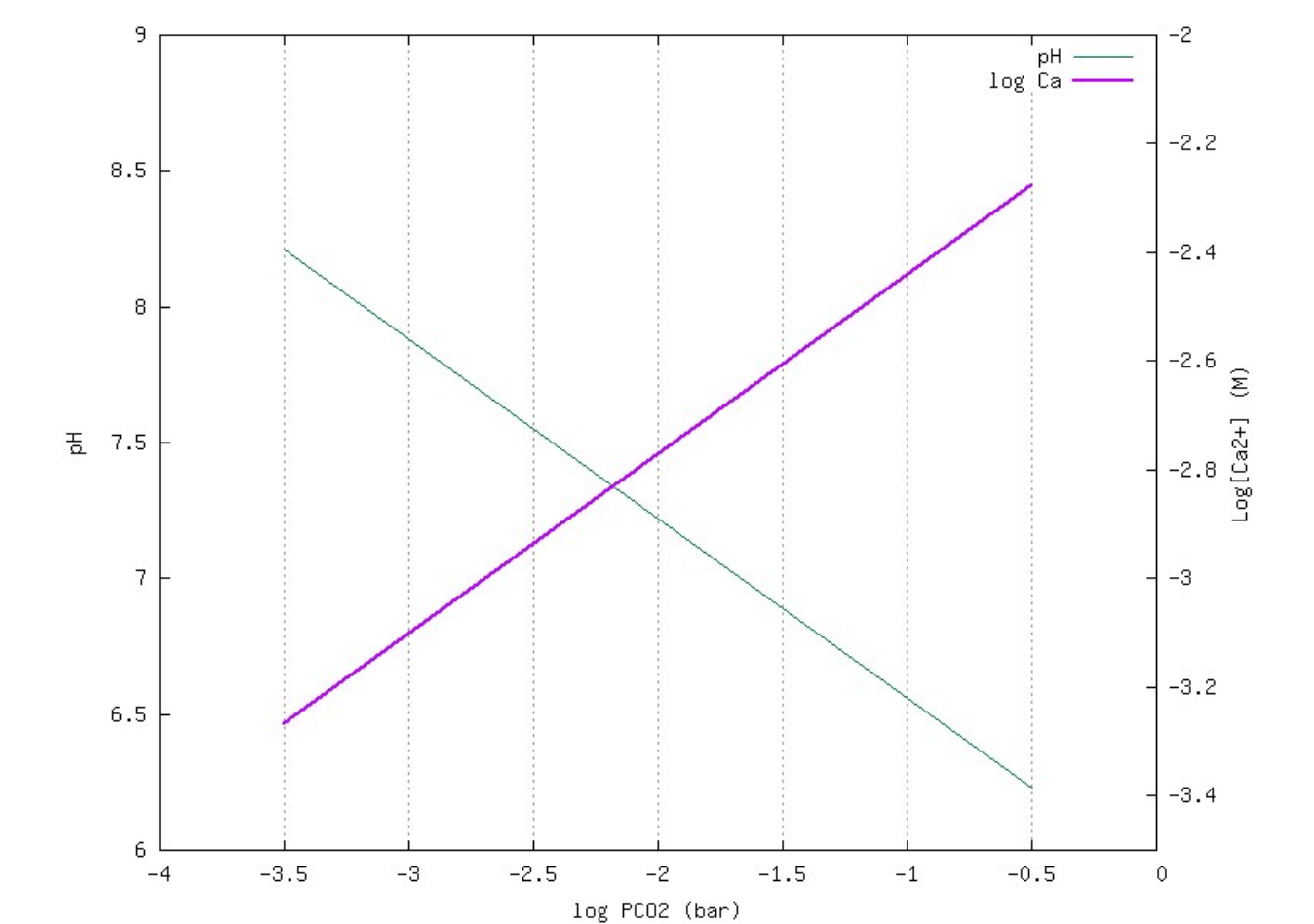
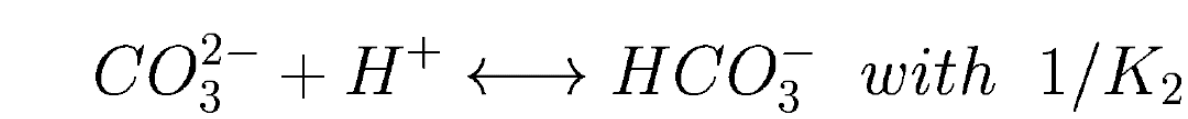
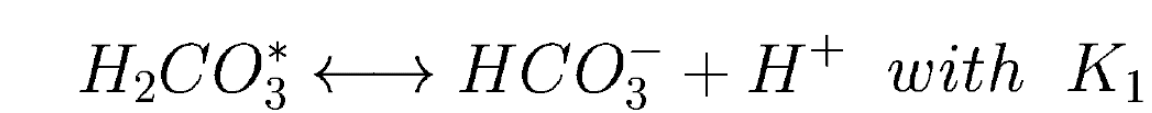
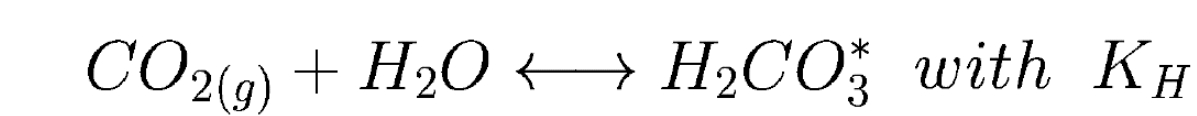
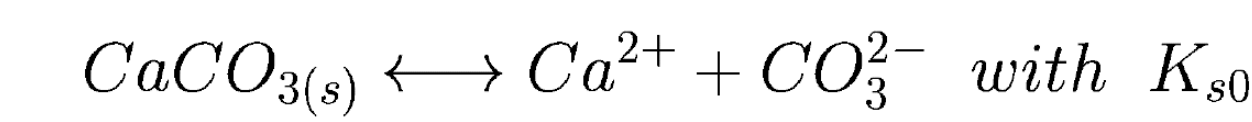


#### Calcite Solubility

The reaction of dissolution/precipitation of calcite can be written like a simple chemical equation:



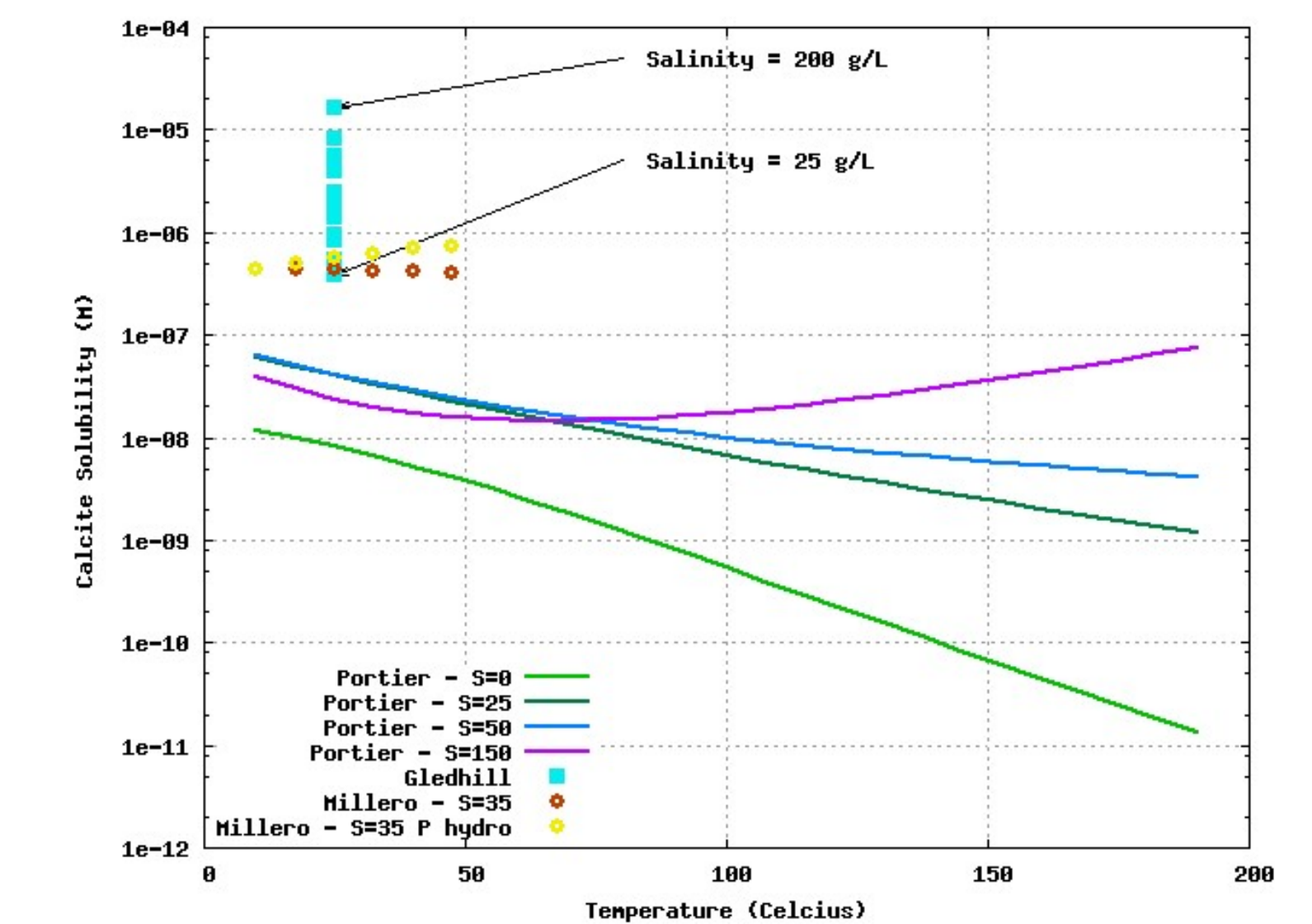
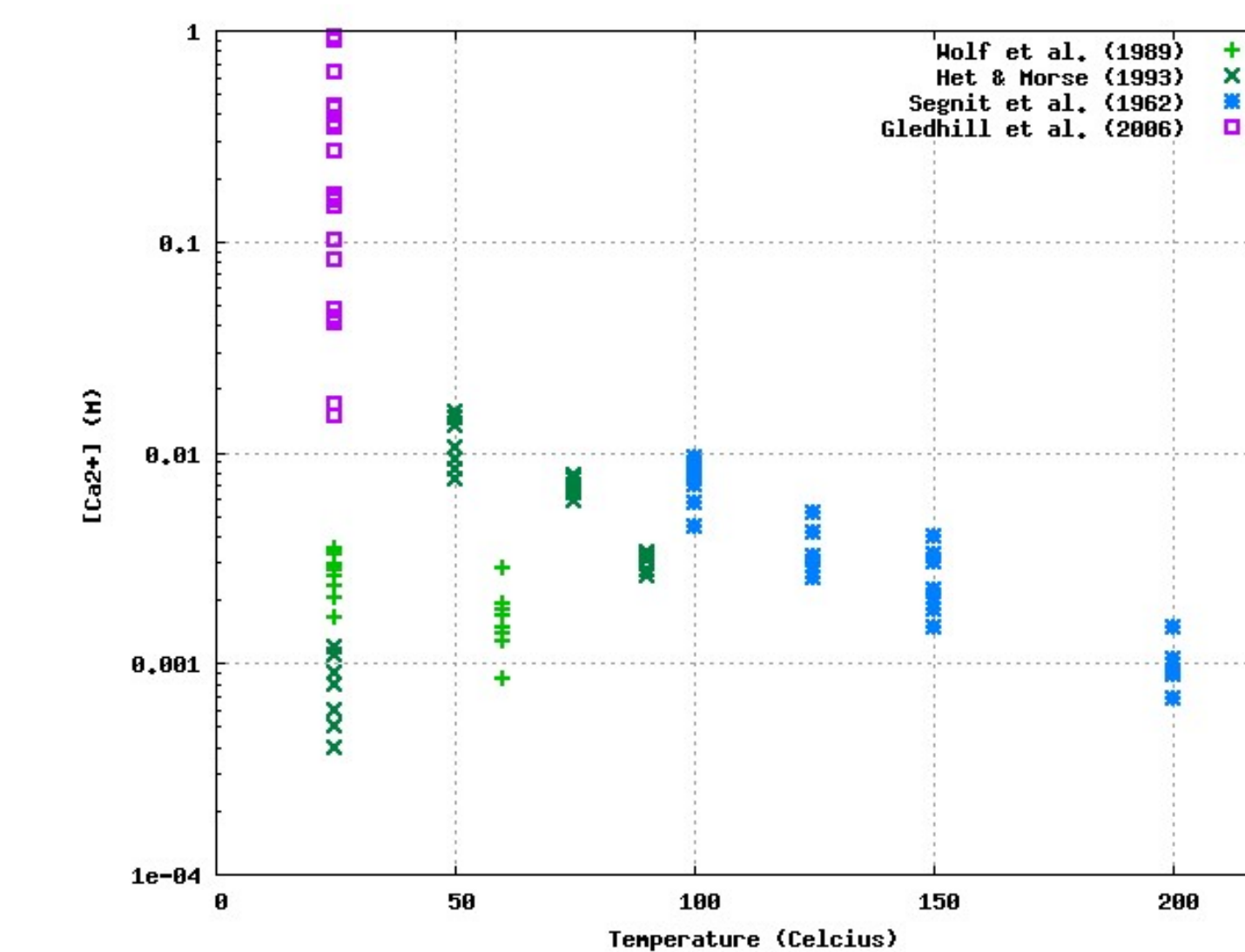
All the species co-exist simultaneously and the concentrations of these ions are not independent but fixed by equilibrium between one another and any present solid phases :



For example neglecting activity coefficient and fugacity coefficient calcium concentration

is linked with CO2 pressure by:  $[Ca^{2+}]^3 \sim \frac{K_1 \cdot K_{s0}}{4K_2 \cdot K_H} \cdot P_{CO_2}$

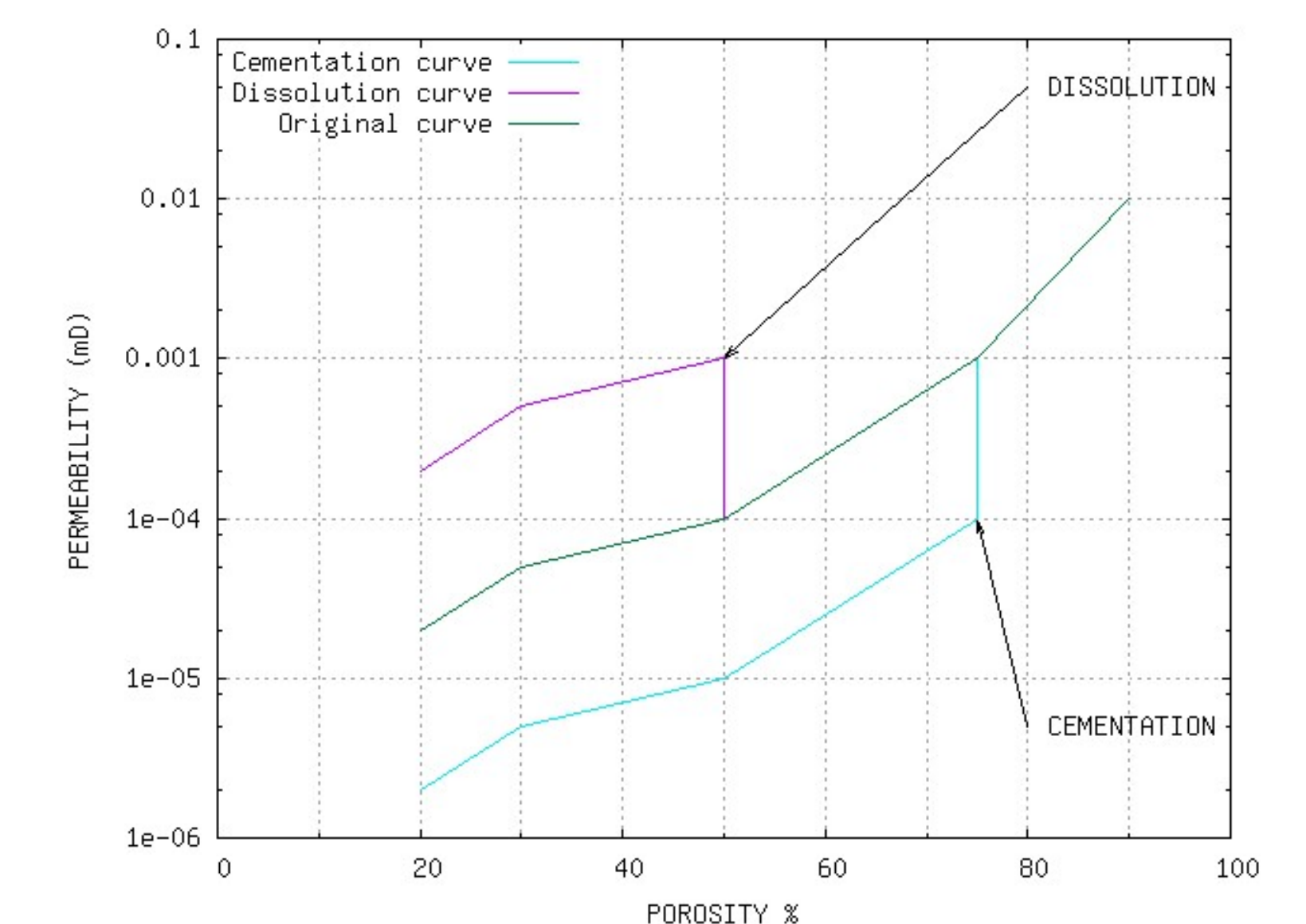
For basinal brines, effects of salinity modify considerably the solubility of calcite and cannot be neglected. Up to now, large discrepancies exist in the geochemical data, particularly for low temperatures (<100°C). We used the solubility function provided by Portier (2005) which can be applied for temperature range 0-300°C, salinity range 0-250 g/L and pressure range 1-100 bar.



Temis3D evaluates Equation {1} with an implicit scheme by a finite volume approach. Temis3D first calculates the flow velocities and T and P distribution in basin strata.

### RETROACTIVE EFFECT ON PERMEABILITY

Even if our geochemical model is quite crude, estimate of porosity changes are used to modify the permeability of the basin formation. We do not use a textural model to calculate permeability variation following cementation or dissolution. We simply shift the porosity/permeability curve used as input by Temis3D by fixing a threshold on cementation/dissolution increments. The threshold is expressed as a percentage of porosity.

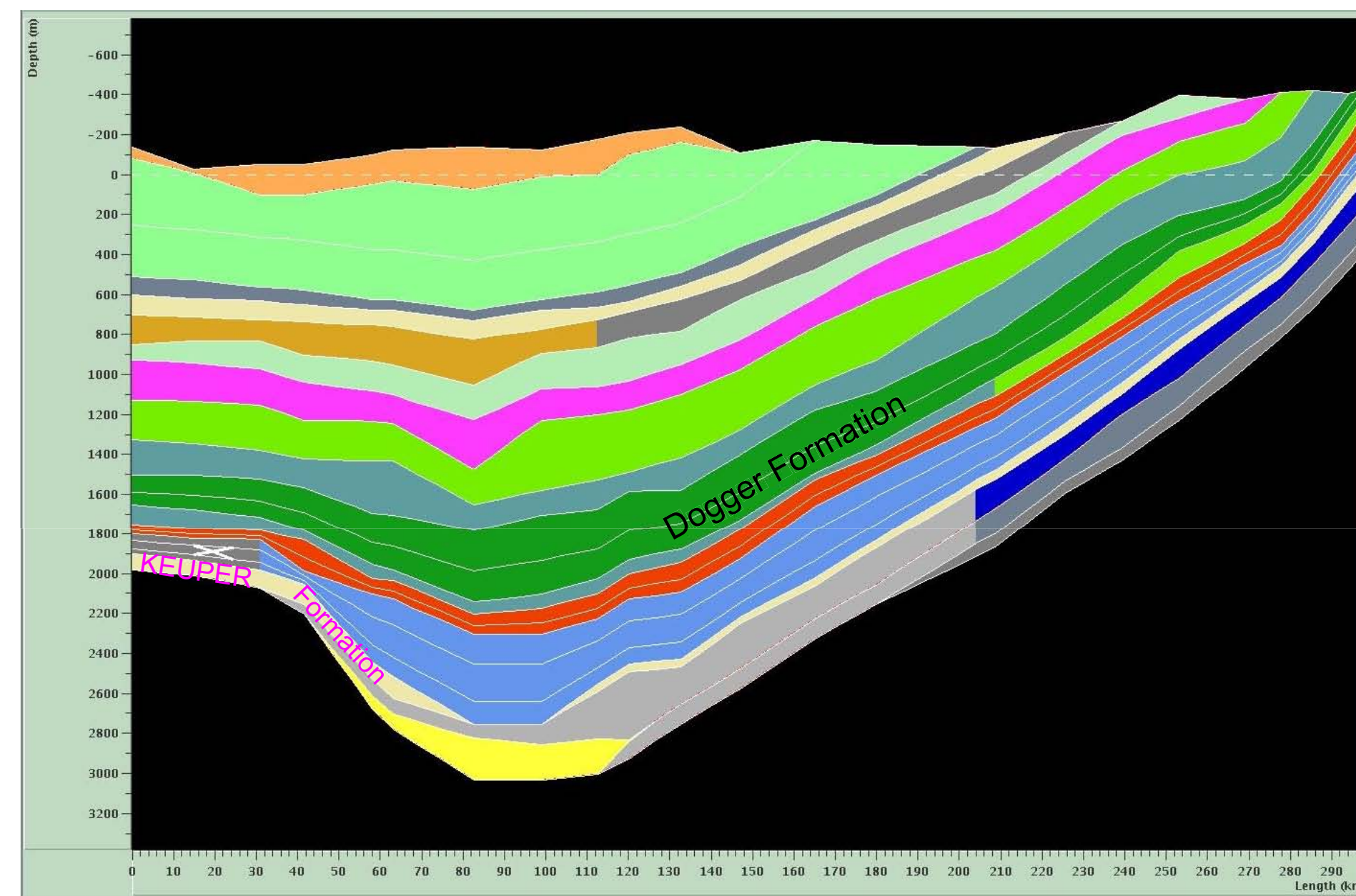




## PARIS BASIN

### Geological history

The Paris Basin is an intracratonic basin with up to 3 km of sedimentary infill deposited on top of Hercynian basement. Sediments range in age from Permian to Quaternary. There are two main permeable petroleum reservoir units in the central part of the Mesozoic of the Paris Basin; the Late Triassic fluvial sandstones (Keuper Formation) and the Middle Jurassic marine carbonates (Dogger Formation). Sandwiched between the Keuper sandstone and the Dogger carbonate are the Liassic (Early Jurassic) shales. These shales are the only major petroleum source rocks within the basin. The basin has experienced a simple burial history punctuated by periods of fairly rapid burial in the Early and Middle Jurassic and Late Cretaceous. Maximum burial occurred in the Oligocene, followed by uplift of variable extent during and following Alpine tectonism. There are several generations of faults within the Paris Basin some of which were inherited from the Palaeozoic basement and were still active in the Tertiary during Pyrenean and Alpine tectonism.



### Diagenetic Episodes

#### Calcite Cementation in Dogger Aquifer

Microthermometric data

$70^{\circ}\text{C} < \text{Th} < 90^{\circ}\text{C}$

Salinity and isotope data show that Dogger formation water contains 15% invasion Keuper water.

Cross formational flow of water occurred like upward flow along faults during the Tertiary (Worden and Matray, 1995)

#### Quartz Cementation in Keuper Aquifer

Microthermometric data

$90^{\circ}\text{C} < \text{Th} < 125^{\circ}\text{C}$

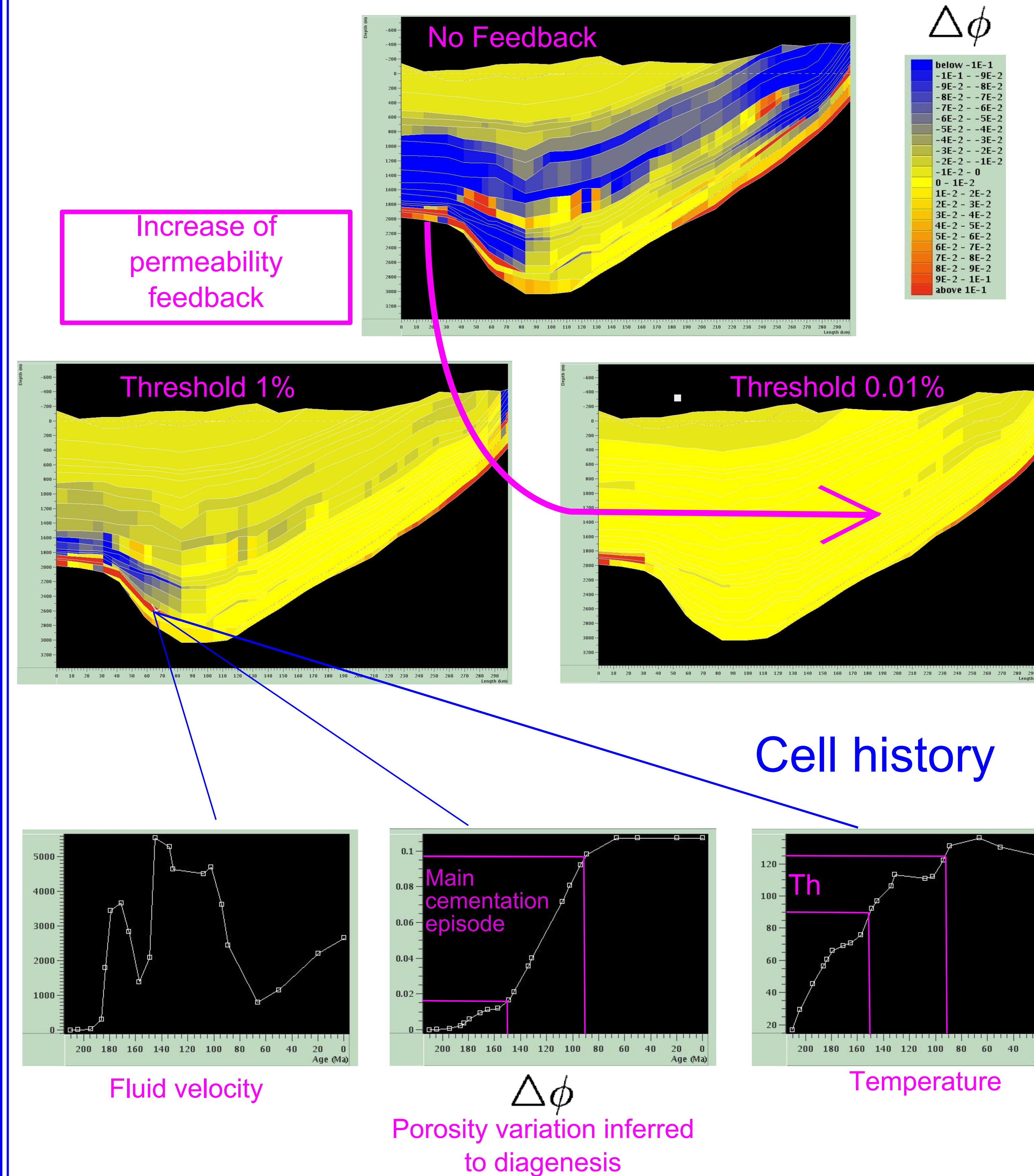
(Guilhaumou, 1993)

Period	Epoch	Stage	Age
Cenozoic	Quaternary	Holocene	
		Pleistocene	Upper, Middle, Lower
		Pliocene	Piacenzian, Zanclean
	Neogene	Miocene	Messinian, Tortonian, Sarravallian
		Oligocene	Langhian, Burdigalian, Aquitanian
		Eocene	Chattian, Rupelian, Priabonian
	Paleogene	Eocene	Barthonian, Lutetian, Ypresian
		Paleocene	Thanetian, Selandian
		Danian	
		Maestrichtian	
Mesozoic	Cretaceous	Upper	Sanctian, Coniacian, Turonian
		Lower	Albian, Aptian, Barremian
	Jurassic	Hauterivian	
		Valanginian	
		Berriasian	

## RESULTS OF SIMULATIONS

### QUARTZ CEMENTATION

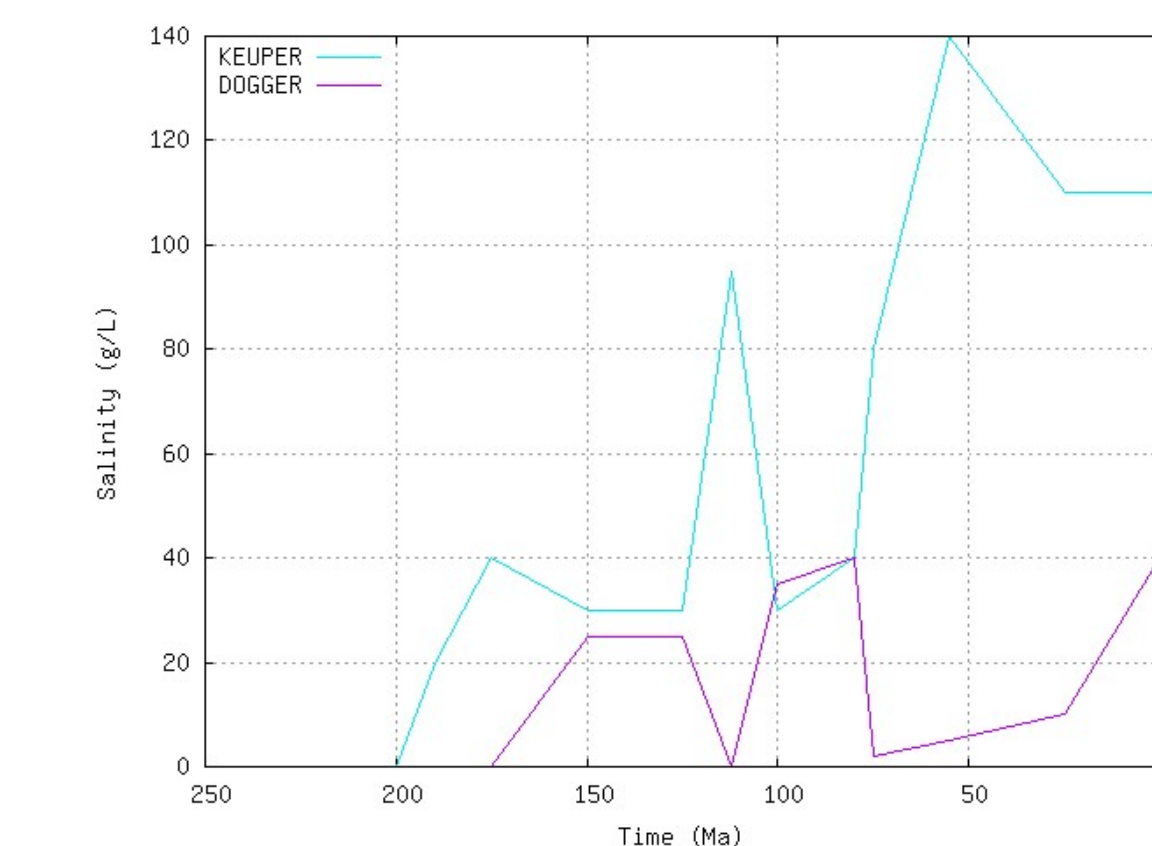
EFFECT of PERMEABILITY FEEDBACK on POROSITY VARIATIONS ASSOCIATED TO QUARTZ DIAGENESIS



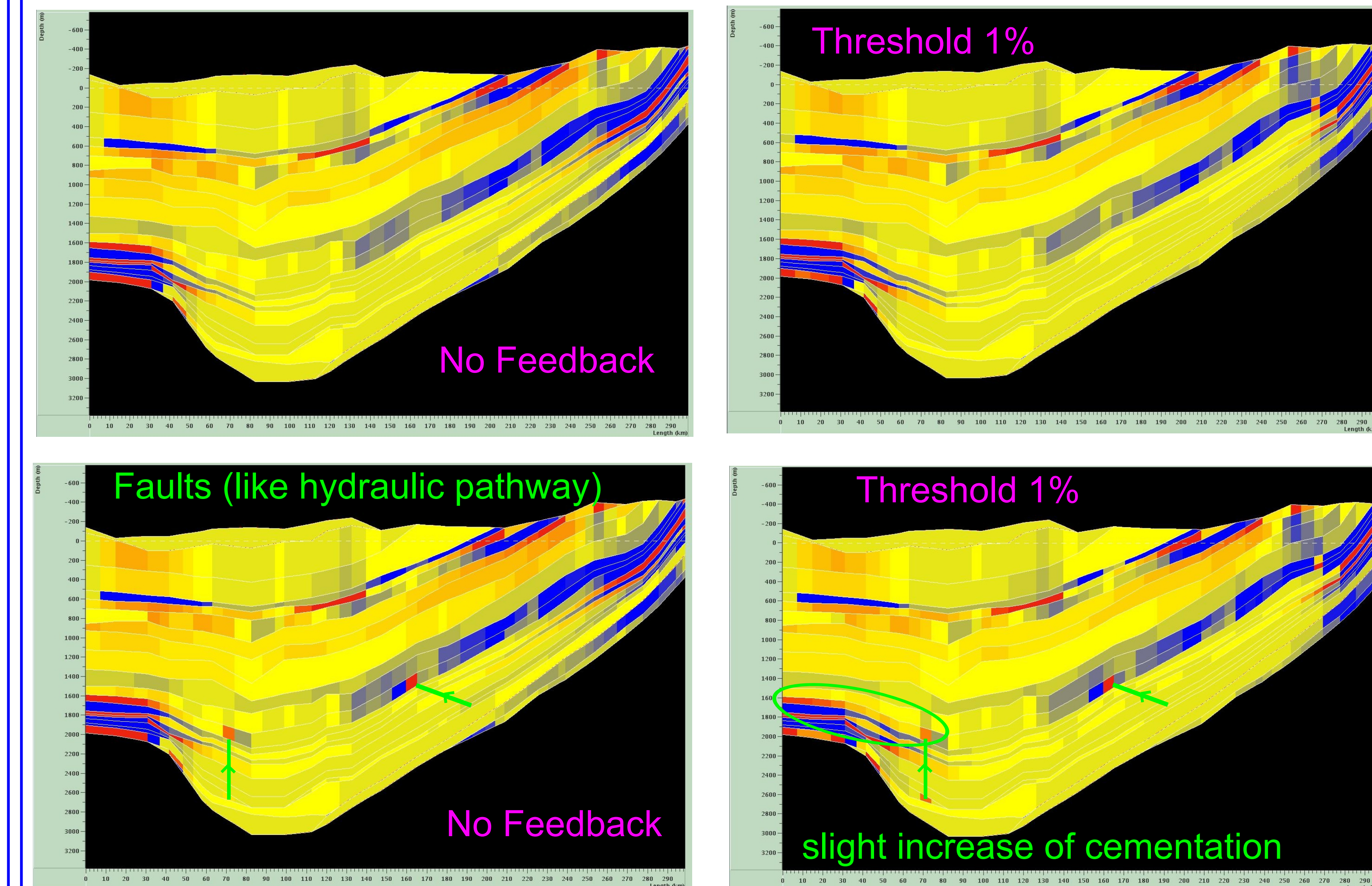
### CALCITE CEMENTATION

#### SALT EFFECT

Evolution of the salinity in the Keuper and in The Dogger aquifers. Results of numerical simulation performed by Gonçalves et al. (2003)



#### EFFECT of FAULT & EFFECT of PERMEABILITY FEEDBACK



However, amount of precipitated calcite is low because of the low solubility. Large uncertainties on solubility product: at  $25^{\circ}\text{C}$ , at least 2 orders of magnitude. Can we multiply amount of precipitated or dissolved mineral by 100 ?

## CONCLUSIONS

We observe a good agreement between our simulations and microthermometric measurements for quartz overgrowth in Keuper aquifer. For calcite cementation, simulations provide good localization of mineral reactions. However quantitative estimates of porosity variations are not obtained. Permeability feedback results in a focusing of mineral reactions.

Our calculations are first step towards reactive transport modelling. Equilibrium assumption provides good results for basin scale simulations; however, estimate of volume changes of minerals rests on accurate solubility data. Use of apparent solubility products accounts for the influence of salinity,  $\text{CO}_2$  pressure, and chemical interactions.

## PERSPECTIVES

Salinity advection, equilibrium thermodynamics calculations for major cations and anions based on Gibbs free energy minimization.

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