Porosity Creation in Carbonate Reservoirs by Pre-Oil Charging With Source-Rock-Derived Corrosive Fluids: 1D/3D-Reactive Mass Transport Modeling*

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Abstract

The origin of locally high porosity in carbonate reservoirs is still a matter of debate. One hypothetical concept is the late diagenetic calcite dissolution caused by acidic corrosive fluids (ACF) which migrated through the reservoir immediately before the actual oil phase. Our hydrogeochemical 1D-reactive mass transport (1DRT) modeling aims to test this concept by providing quantitative evidence based on the principles of chemical equilibrium thermodynamics and reactive mass transport. Such 1DRT calculations link 1D-purely advective pore-water flow with the equilibrium thermodynamics of water-rock-gas interactions. Our motivation comes from the work of Ehrenberg et al. (2012) about dissolution of micritic calcite in Middle East oil fields and from their conclusions that (1) "diagenetic reactions must be constrained geochemically", and (2) that "the theory about dissolution by acid pore water has produced significant net increases in bulk porosity has not been supported by models of mineral solubility and fluid flow". Our modeling results reveal that the calcite solubility in the system "ACF/calcite/$CO_2(g)$" increases along with decreasing pressure/temperature. During their migration, ACF may reach saturation with respect to calcite (e.g., at 305 atm and 85°C) before they enter the carbonate reservoir. Although saturated with respect to calcite, further migration of such ACF through the reservoir into areas of lower pressure/temperature (e.g., 295 atm and 82°C) causes undersaturation of ACF with respect to calcite. Consequently, such migrating ACF dissolve calcite until the saturation is re-established again (e.g., 295 atm and 82°C). Thus, thermodynamically controlled and repeated chemical re-equilibration among ACF, calcite, and $CO_2(g)$ during ACF migration from higher to lower pressure/temperature conditions is the driving force for

continuous calcite dissolution. This continuous calcite dissolution along the flow path of ACF is the inevitable consequence of the chemical-thermodynamic behavior of the system "ACF/calcite/CO_2(g)" under decreasing pressure/temperature –at least in the modeled p/T range from 295 atm/82°C to 205 atm/55°C. This holds also true for dolomitic reservoir rocks. Such self-propagating calcite dissolution before or during migration of the oil phase can increase reservoir porosity and permeability to a certain extent. In contrast, intense ACF-induced calcite dissolution may also lead to a local structural breakdown of the calcite matrix.

References Cited

Ehrenberg, S.N., O. Walderhaug, and K. Bjørlykke, 2012, Carbonate porosity creation by mesogenetic dissolution: Reality or illusion?: AAPG Bulletin, v. 96/2, p. 217–233.

Lambert, L., C. Durlet, J.-P. Loreau, and G. Marnier, 2006, Burial dissolution of micrite in Middle East carbonate reservoirs (Jurassic–Cretaceous): Keys for recognition and timing: Marine and Petroleum Geology, v. 23, p. 79–92.

Parkhurst, D.L., and C.A.J. Appelo, 2013, Description of input and examples for PHREEQC version 3--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p. Website accessed September 30, 2015, http://pubs.usgs.gov/tm/06/a43/.

Parkhurst, D.L., K.L. Kipp, and S.R. Charlton, 2010, PHAST Version 2 - A program for simulating groundwater flow, solute transport, and multicomponent geochemical reactions: U.S. Geological Survey Techniques and Methods 6-A35, 235 p. Website accessed September 30, 2015, http://pubs.usgs.gov/tm/06A35/pdf/TM6-A35.pdf.

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Porosity Creation in Carbonate Reservoirs by Pre-Oil Charging with Source-Rock-Derived Corrosive Fluids: 1D/3D-Reactive Mass Transport Modeling
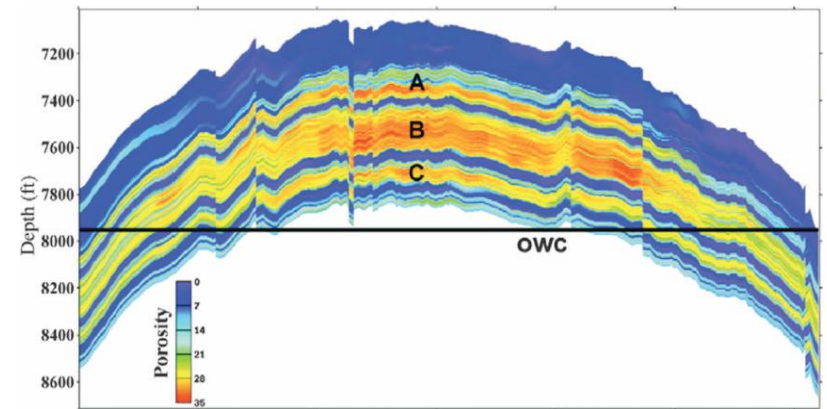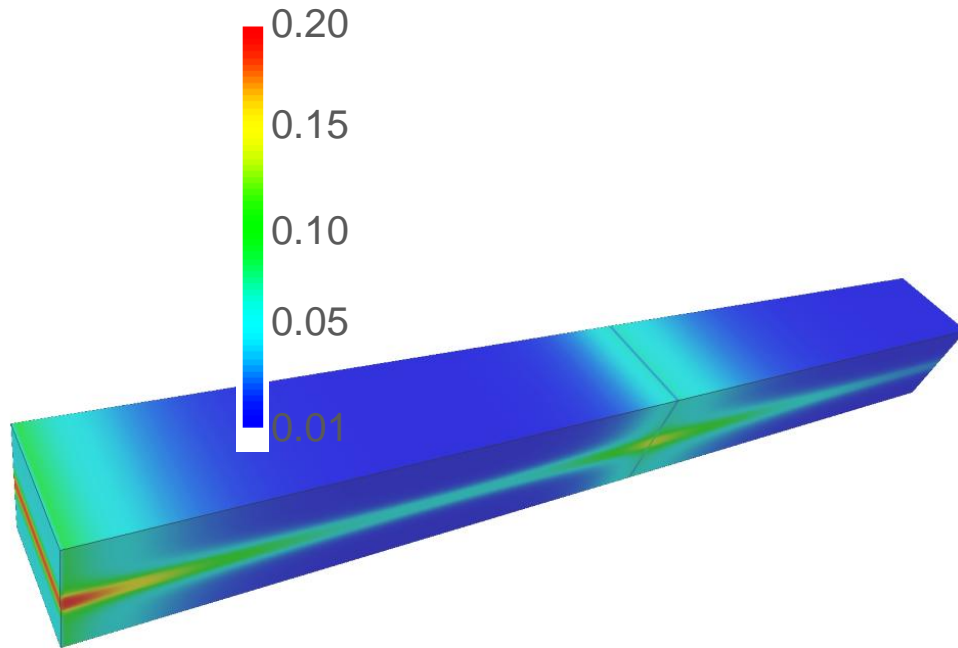
Lambert et al. (2006)

Ehrenberg et al. (2012)

Water **i**n **P**etroleum **S**ystems

W. van Berk, Y. Fu, and H.-M. Schulz

TU Clausthal
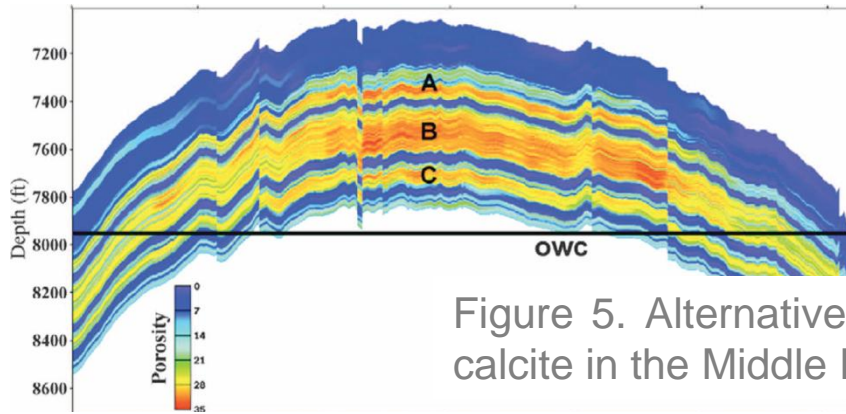Clausthal University of Technology

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POTSDAM

Figure 5. Alternative models for dissolution of microporous micritic calcite in the Middle East oil fields studied by *Lambert et al.* (2006).

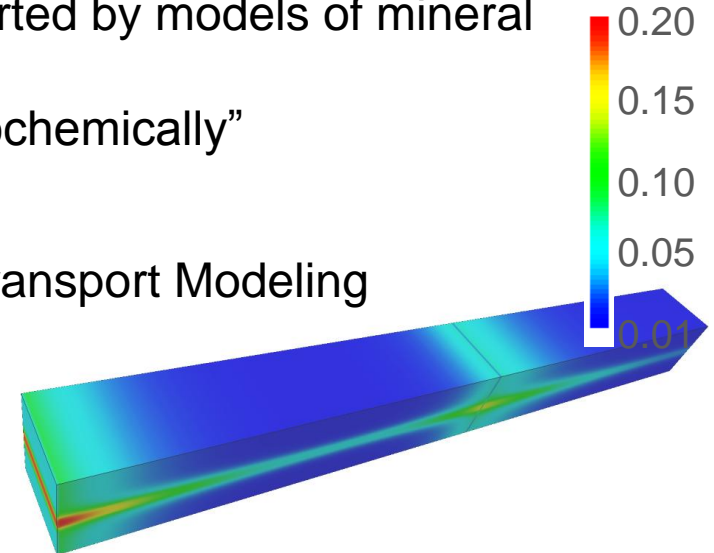**Carbonate porosity creation by mesogenetic dissolution: Reality or illusion?**
Ehrenberg et al., 2012

Their conclusions:
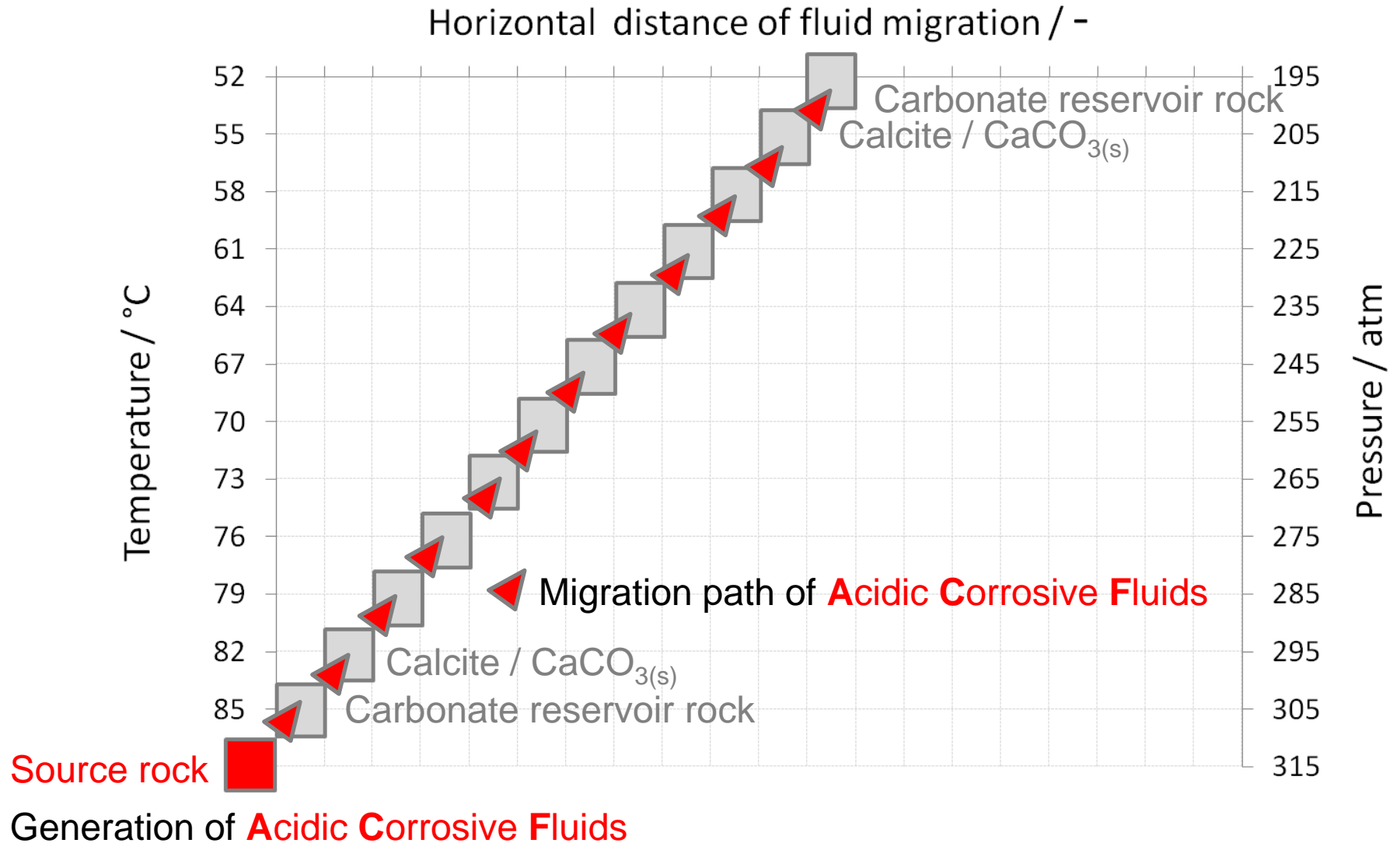(i) "the theory about dissolution by acid pore water has produced significant net increases in bulk porosity has not been supported by models of mineral solubility and fluid flow"
(ii) "diagenetic reactions must be constrained geochemically"

Our aim:
(i) to test this theory by 1D/3D Reactive Mass Transport Modeling
(ii) to identify potential mechanisms & reasons
(iii) to provide quantitative arguments

Horizontal distance of fluid migration / -

Temperature / °C

Pressure / atm

Carbonate reservoir rock
Calcite / CaCO$_{3(s)}$

◄ Migration path of **A**cidic **C**orrosive **F**luids

Calcite / CaCO$_{3(s)}$
Carbonate reservoir rock

Source rock

Generation of **A**cidic **C**orrosive **F**luids

Batch modeling reactor / Siliciclastic source rock

Quartz	0.48 mol
Kaolinite	0.48 mol
Calcite	0.01 mol
Anorthite	0.01 mol
Albite	0.01 mol
K-feldspar	0.01 mol
$CH_{4(g)}$	0.0 mol
$CO_{2(g)}$	0.0 mol
$H_{2(g)}$	0.0 mol

Products of kerogen maturation & oil degradation
$1.9\ CO_2 + CH_4 + 5\ H_2 + 0.1\ CH_3COOH$

PhreeqC 3.pqi

USGS
science for a changing world
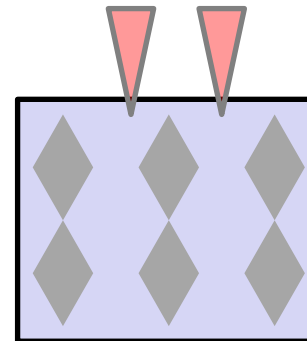
Parkhurst & Appelo (2013)

1.0 m NaCl solution; 1.0 kgw

$T = 88°C$ / $p_{tot} = 315\ atm$

Kerogen maturation (*Helgeson et al.*, 2008)

$C_{292}H_{288}O_{12}(c)(kerogen) = 1.527\ C_{128}H_{68}O_7\ (mature\ kerogen)$
$+ 10.896\ C_{8.8}H_{16.9}\ (crude\ oil) + 0.656\ CO_2$
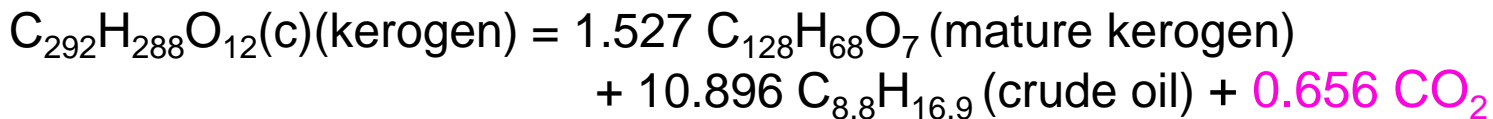
Hydrolytic disproportionation / Oil degradation (*Seewald*, 2003)

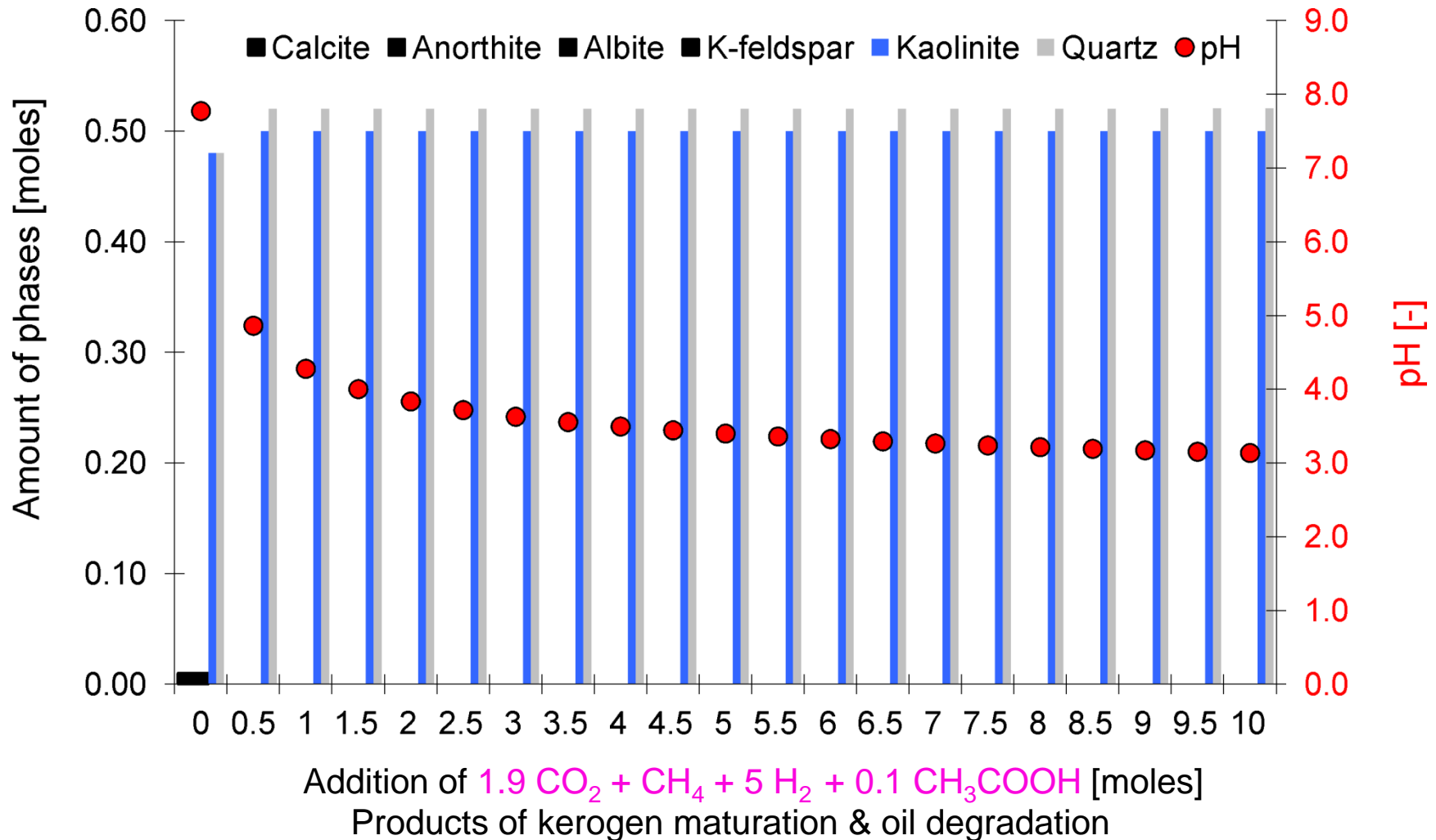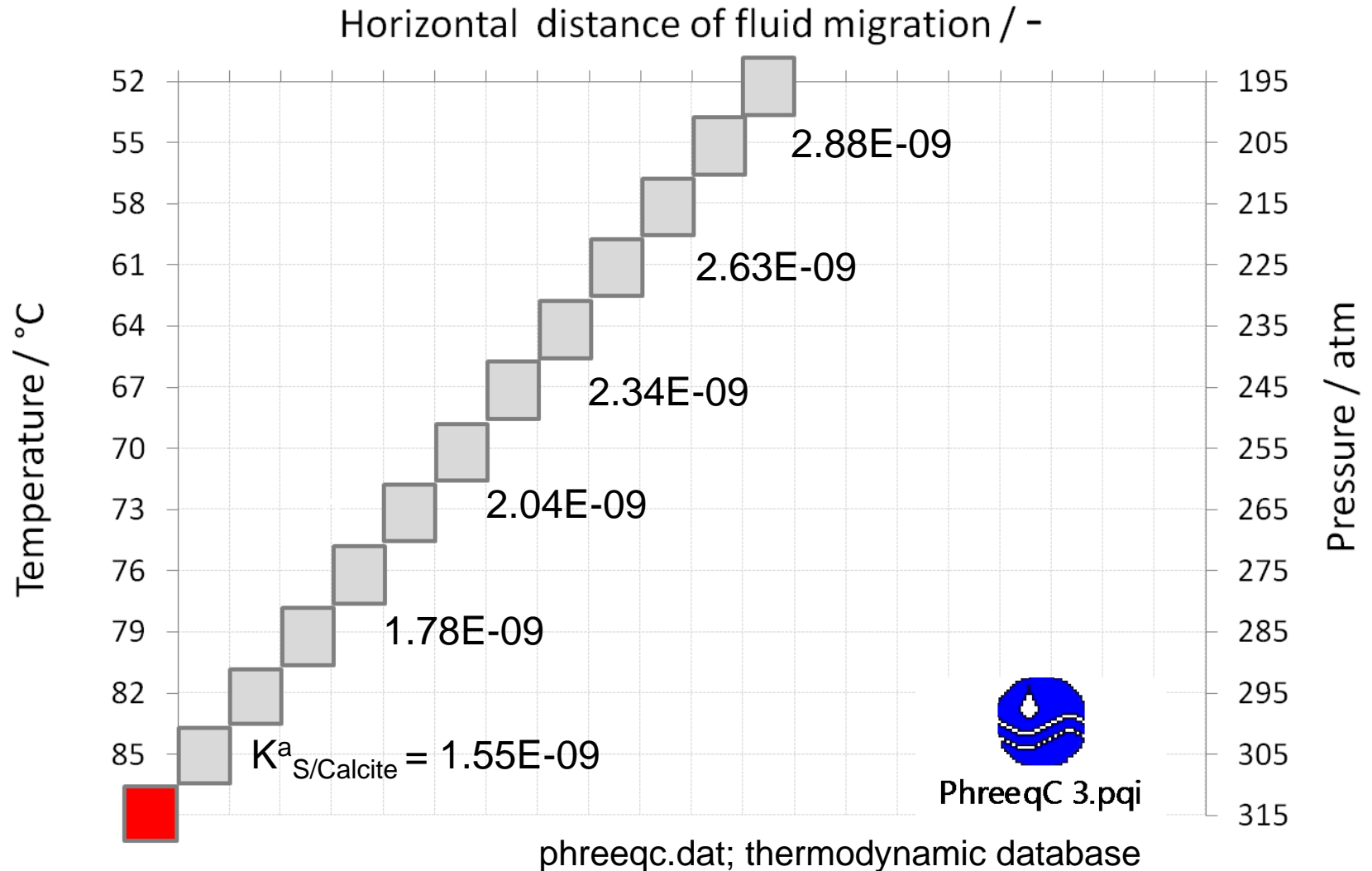$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 4\ H_2O \rightarrow R + 2\ CO_2 + CH_4 + 5\ H_2\ (+ CH_3COOH)$

Water-rock-gas interactions lead to the formation of Acidic Corrosive Fluids (ACF)

Siliciclastic source rock

Water-rock-gas interactions lead to the formation of Acidic Corrosive Fluids (ACF)

Addition of 1.9 CO_2 + CH_4 + 5 H_2 + 0.1 CH_3COOH [moles]
Products of kerogen maturation & oil degradation

$$CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}; K^a_{S/Calcite}, [mol\ kgw^{-1}]$$

Horizontal distance of fluid migration / -

2.88E-09

2.63E-09

2.34E-09

2.04E-09

1.78E-09

$K^a_{S/Calcite} = 1.55E-09$

Temperature / °C

Pressure / atm

PhreeqC 3.pqi

phreeqc.dat; thermodynamic database

Carbonate reservoir rock

$$CaCO_{3(s)} = Ca^{2+} + CO_3^{2-}; K^a_{S/Calcite}$$
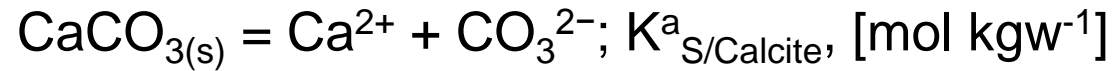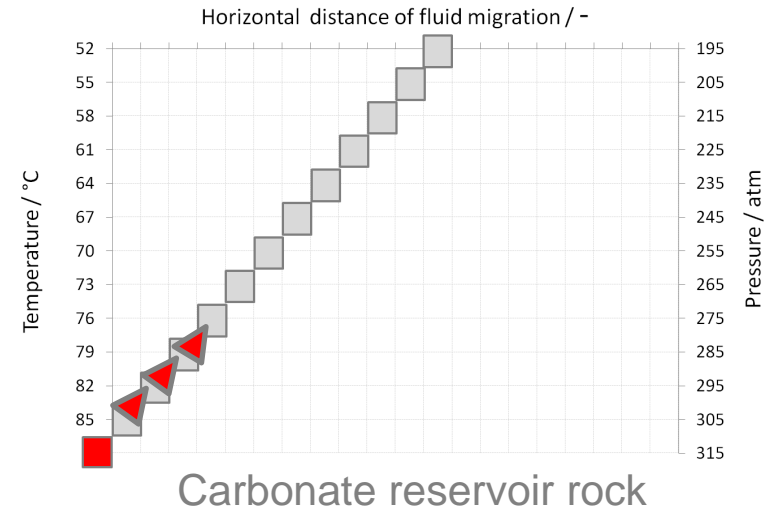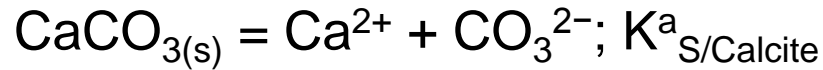
plus 2 additional solubility equilibrium reactions; potential secondary minerals
- quartz
- kaolinite

plus 3 additional solubility equilibrium reactions; potential multi-component gas
- $CH_{4(g)}$
- $CO_{2(g)}$
- $H_{2(g)}$

plus 18 additional equilibrium reactions; aqueous species
- $HCO_3^-{}_{(aq)}$
- $CaHCO_3^+{}_{(aq)}$
- $CO_{2(aq)}$
- $NaHCO_{3(aq)}$
-

Σ = 24 equilibrium reactions

Calculating mass transfer and equilibrium species distribution

10.0 atm $pCO_{2(g)}$

1.0 m $NaCl_{(aq)}$

$Calcite_{(s)}$

85°C / 305 atm   *versus*   **55°C / 205 atm**
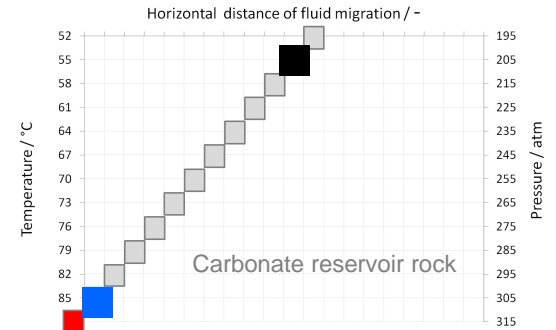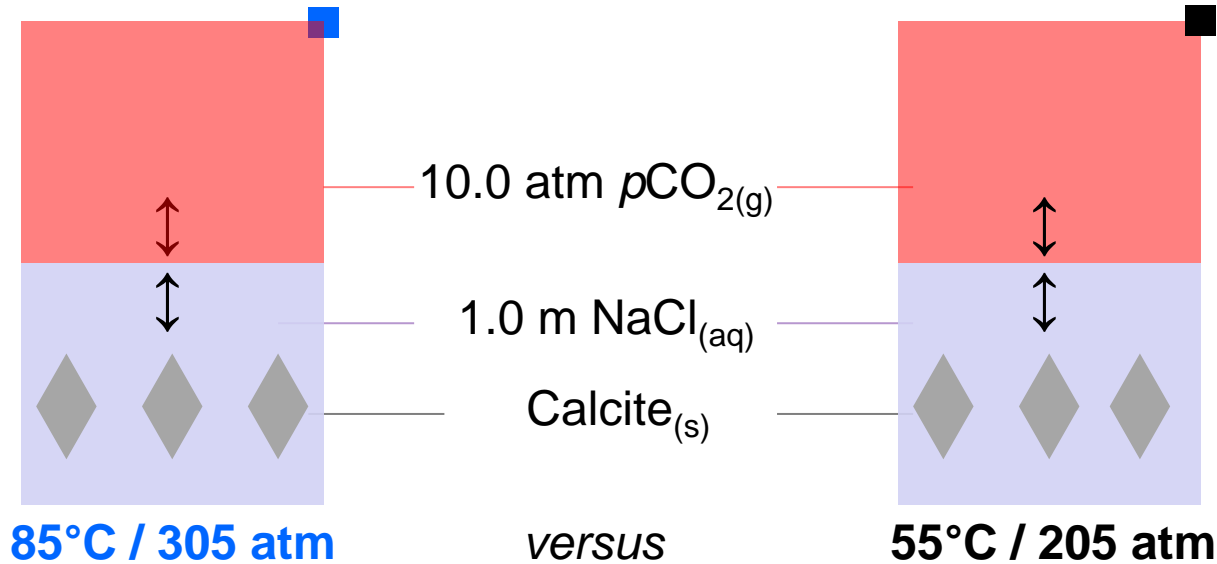
15.4	23.8	Dissolved calcite [mmol kgw^{-1}]
5.52	5.47	pH [-]

Horizontal distance of fluid migration / -

Temperature / °C

Pressure / atm

Carbonate reservoir rock

Σ = 24 equilibrium reactions
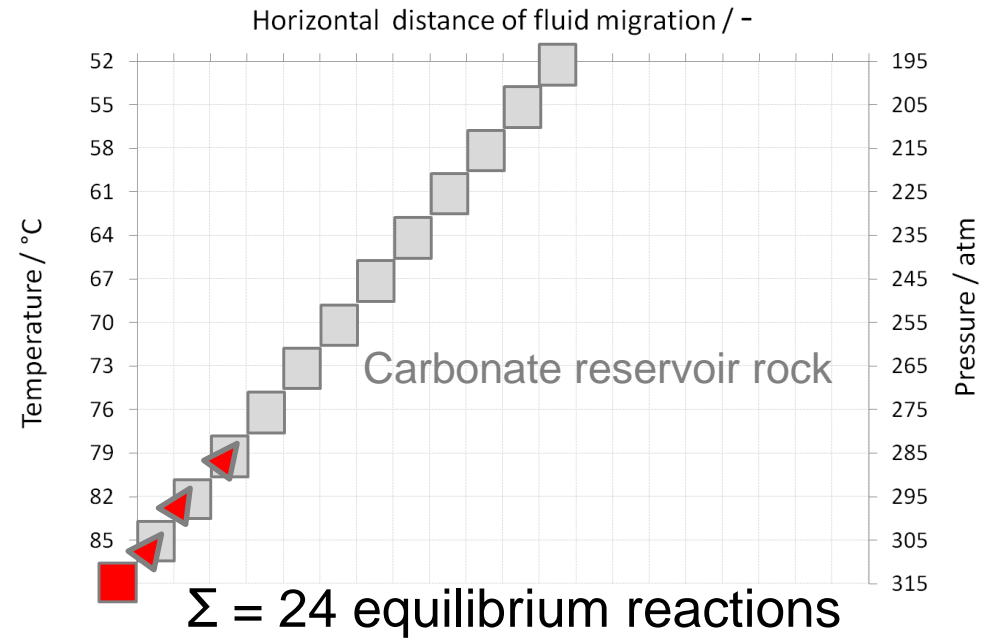
Calcite dissolution along the migration path of ACF
is the inevitable consequence of chemical-thermodynamics

PhreeqC 3.pqi

Horizontal distance of fluid migration / -

593 / 5.07

588 / 5.05

581 / 5.04

572 / 5.02

562 / 5.01

549 / 4.99

536 / 4.98

521 / 4.97

506 / 4.96

3295 g liter^{-1} PV / pH 4.95 (n = 1000)

ACF (pH 4.90) gets saturated regarding calcite

Temperature / °C

Pressure / atm

Source rock

n = pore volume exchange

Horizontal distance of fluid migration / -

593 / 5.07 Φ_{new}: 0.12

$\Phi_{initial}$: 0.10

Vtotal: 10.0 liter

PV: 1.0 liter

VCc: 9.0 liter

MCc: 24.3 kg

VCc$_{dissolved}$: 1.22 liter

Φ_{new}: 0.22

3295 g liter^{-1} PV / pH 4.95 (n = 1000)

(i) Temperature / pressure regime

Amount of dissolved calcite; n = 1000

3295 g liter^{-1} PV

506

593

ACF migration path

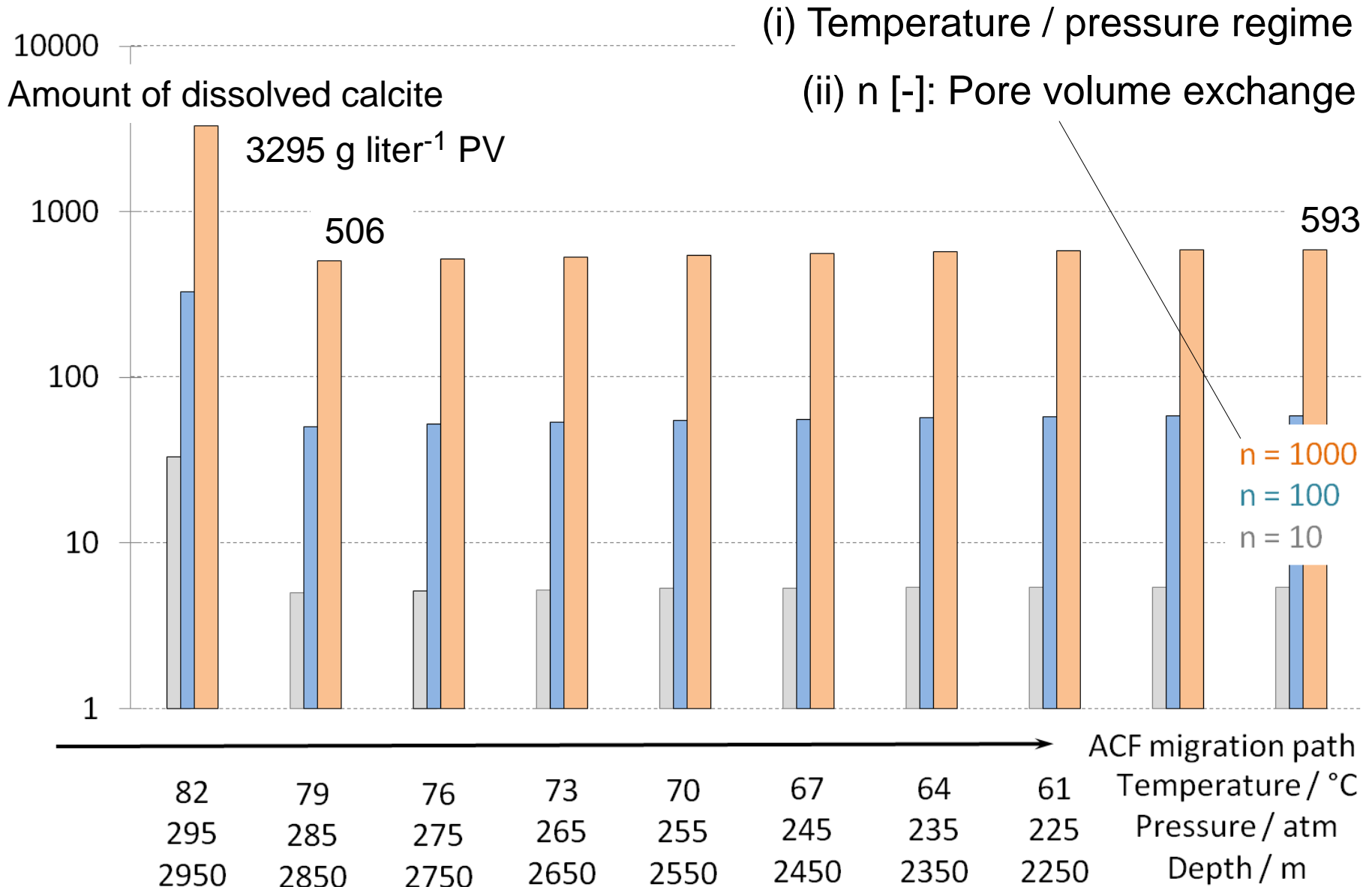|								
82	79	76	73	70	67	64	61	Temperature / °C
295	285	275	265	255	245	235	225	Pressure / atm
2950	2850	2750	2650	2550	2450	2350	2250	Depth / m

(i) Temperature / pressure regime

(ii) n [-]: Pore volume exchange

Amount of dissolved calcite

3295 g liter^{-1} PV

506

593

n = 1000
n = 100
n = 10

ACF migration path

Temperature / °C	Pressure / atm	Depth / m
82	295	2950
79	285	2850
76	275	2750
73	265	2650
70	255	2550
67	245	2450
64	235	2350
61	225	2250

Horizontal distance of fluid migration / -

593 / 5.07

588 / 5.05

581 / 5.04

572 / 5.02

562 / 5.01

549 / 4.99

536 / 4.98

521 / 4.97

506 / 4.96

3295 g liter^{-1} PV / pH 4.95 (n = 1000)

ACF (pH 4.90) gets saturated regarding calcite

Source rock

n = pore volume exchange

(iii) Intensity of ACF release

1.0 mol ACF

0.1 mol ACF

10.0 mol ACF

Amount of dissolved calcite
g liter^{-1} PV

Products of kerogen maturation & oil degradation

Source Rock
- kerogen maturation
- oil degradation

10000

1000

100

10

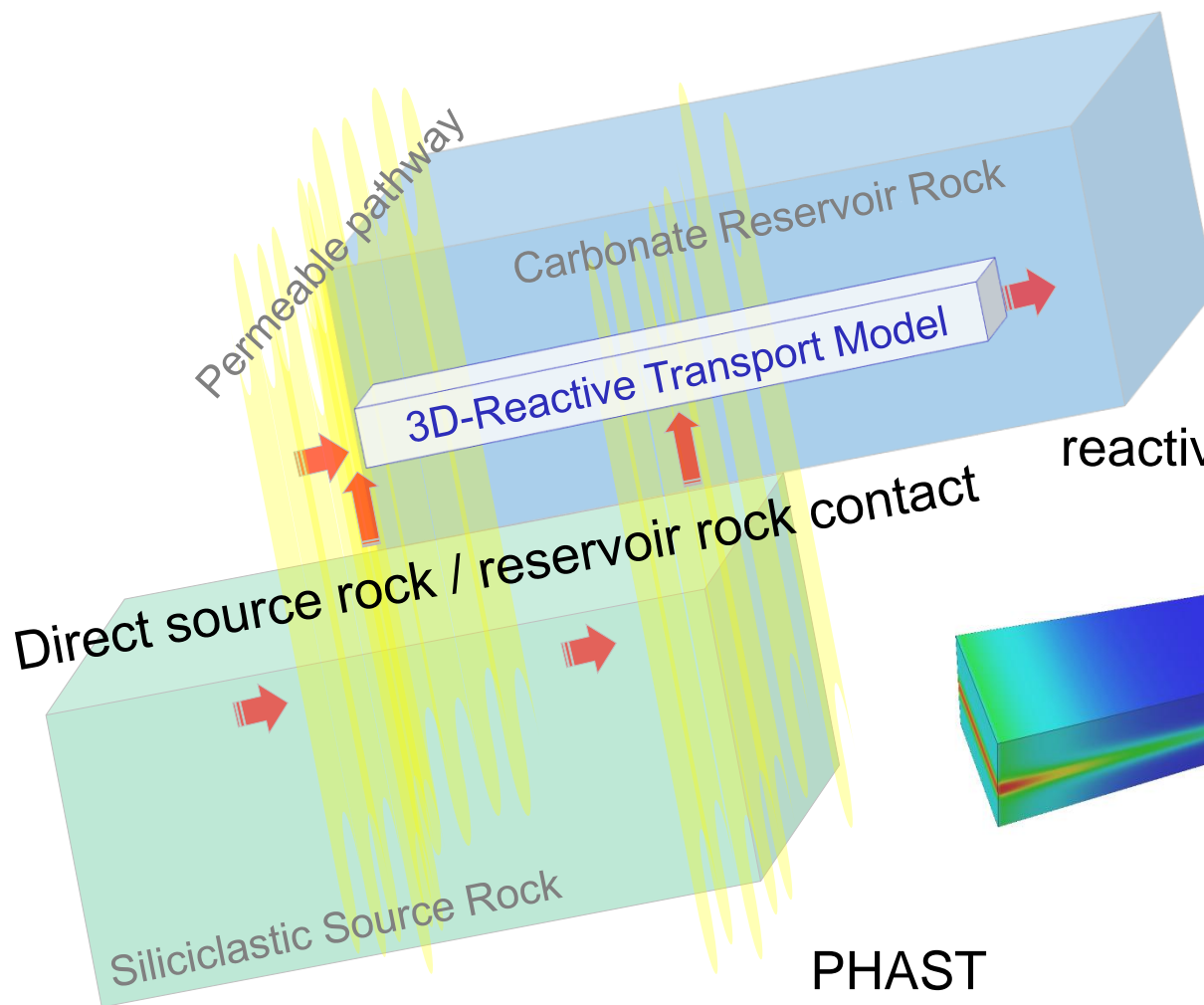1

82
295
2950

10000

1000

100

10

1

82
295
2950

10000

1000

100

10

1

82
295
2950
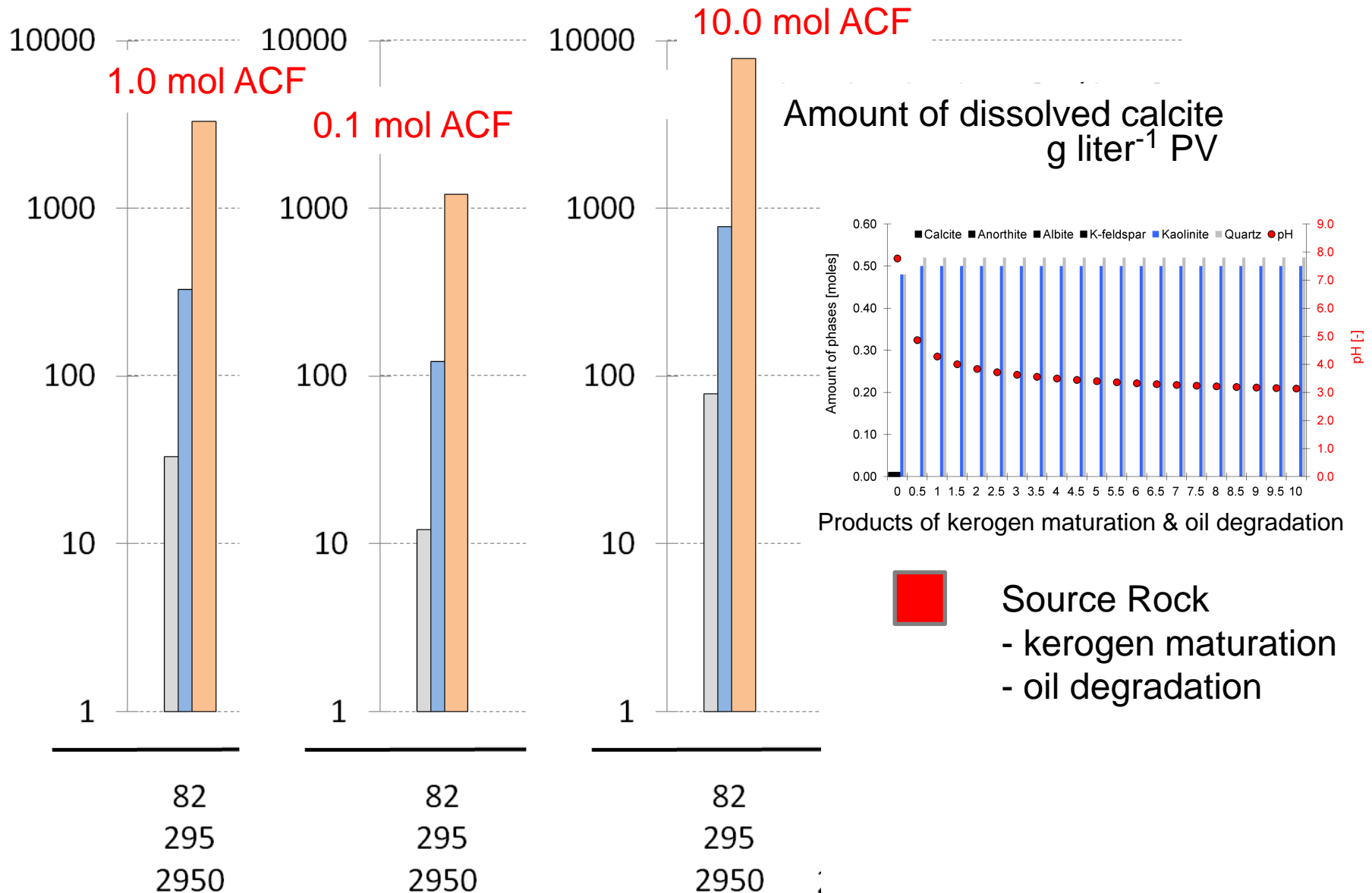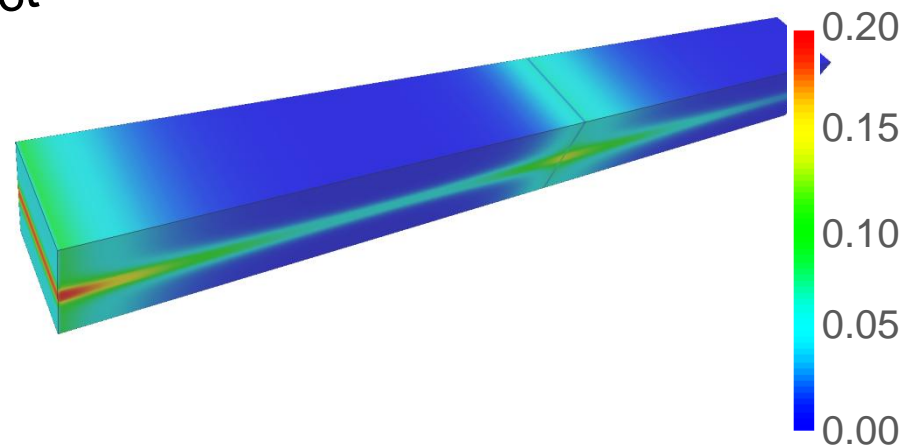
3D hydrogeochemical
reactive mass transport modeling

PHAST

Version 2—A Program for Simulating Groundwater Flow,
Solute Transport, and Multicomponent Geochemical Reactions
(Parkhurst, Kipp, and Charlton, 2010)

PHREEQC.phrq

PhreeqC 3.pqi

van Berk, W., Y. Fu & H.-M. Schulz (2015)
Creation of Pre-Oil Charging Porosity by Migration of Source Rock-Derived
Corrosive Fluids through Carbonate Reservoirs: One-dimensional Reactive
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Petroleum Geoscience, Vol. **21**, pp. 35–42
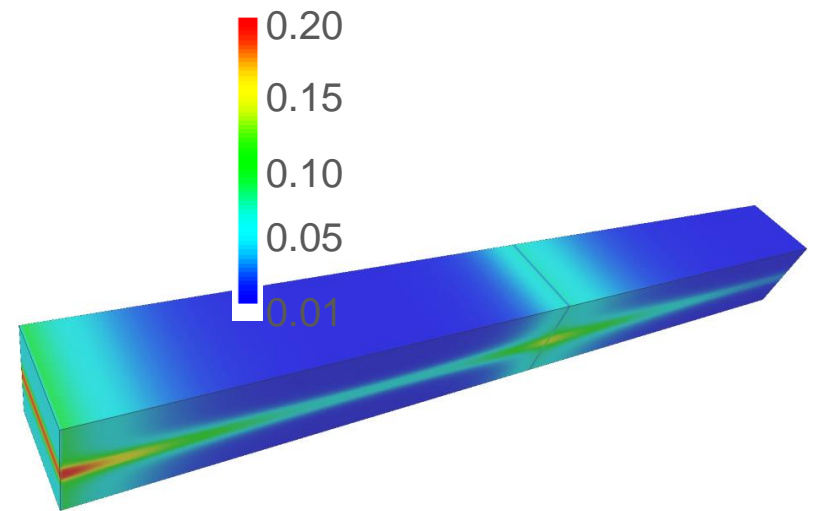
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