# $CO_2$QUEST

## Potential Impact of Selected Impurities on Geochemistry Related to $CO_2$ Storage

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* slides + presentation

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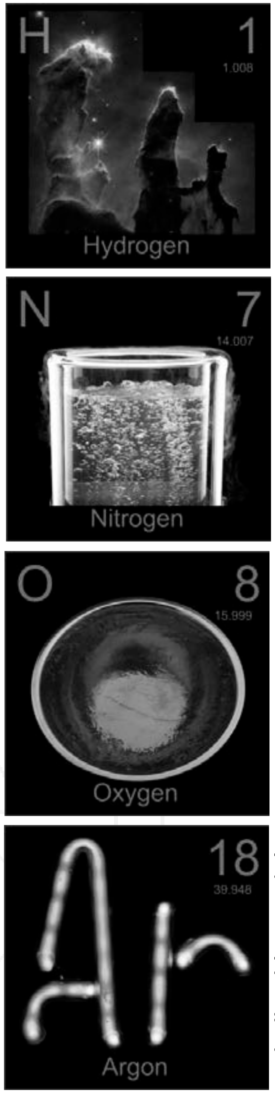
# impact of impurities – physics

## impact of non-condensible gases

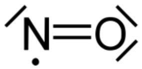
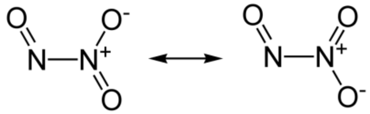
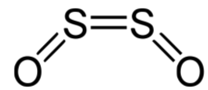
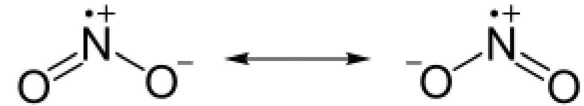
- **changing physical properties of $CO_2$**
  **mobility, density, wettability**
  → **injectivity**

- **use of pore space**
  → **smaller storage volume for $CO_2$**

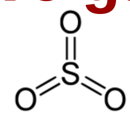


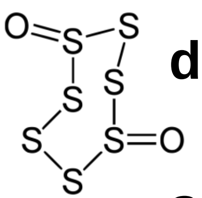

periodictable.com/Elements

# impact of impurities – chemistry

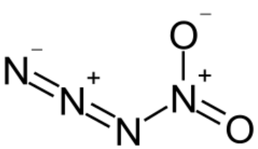
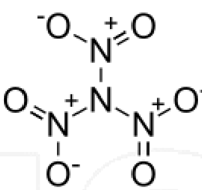
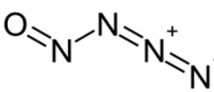





## impact of chemically active gases – $H_2S$, $NO_x$, $SO_x$

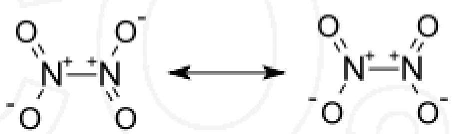
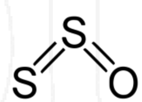


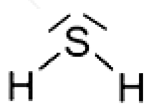
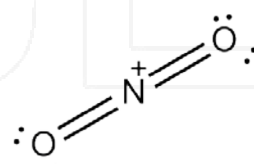
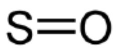


- **acidification around the well**
  **dissolution of carbonates**

- **acidification in greater distances**
  **precipitation of secondary minerals**

de.wikipedia.org/

# impact of impurities – chemistry

**impact of chemically active gases – $H_2S$, $NO_x$, $SO_x$**

- **acidification around the well**
  **dissolution of carbonates**

- **acidification in greater distances**
  **precipitation of secondary minerals**

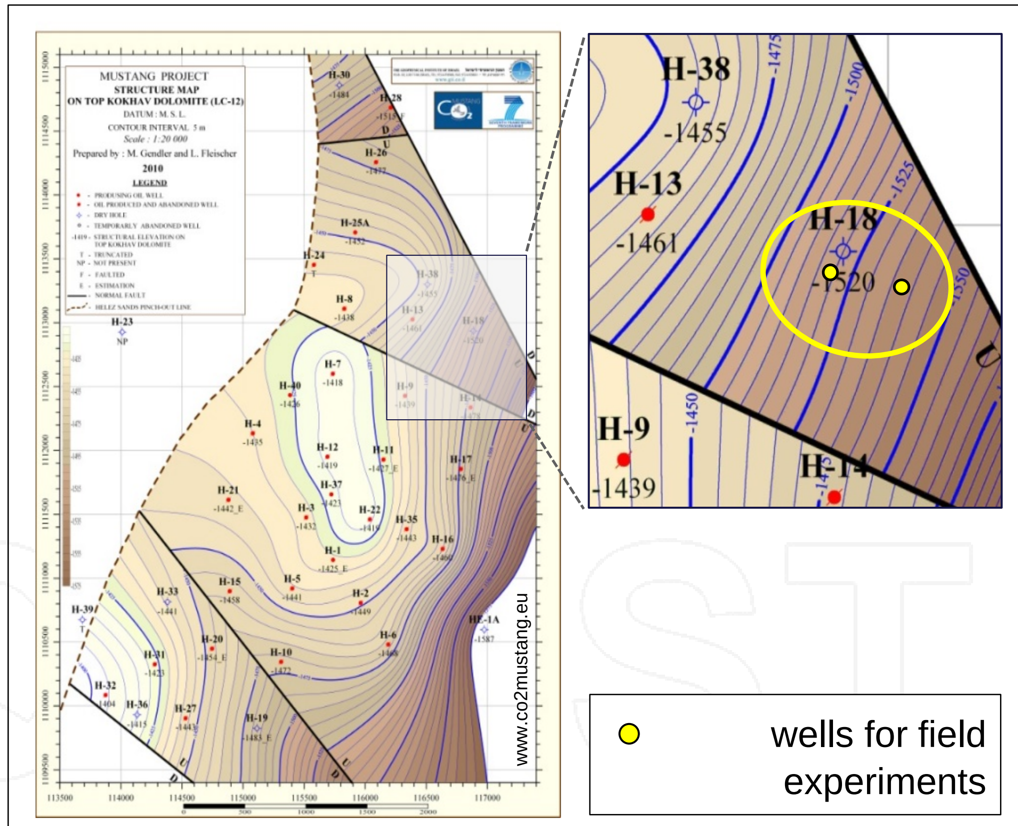

de.wikipedia.org/

# Heletz site

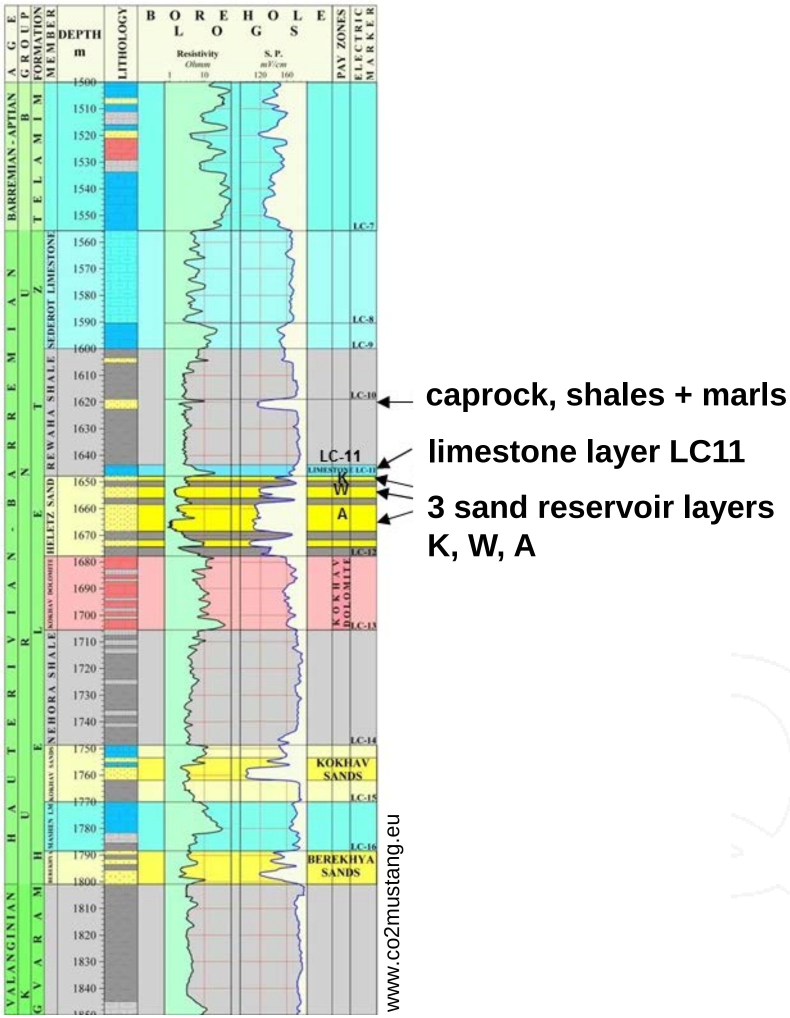
**field scale experiment**

**Southern Mediterranean Coastal Plain of Israel**

**saline water on edges of depleted oil field**



## reservoir structure




www.co2mustang.eu

anticlinal structure

thickness of target horizon approx. 20 m

3 conductive, Lower Cretaceous sandstones K,W, A with cumulative thickness of approx. 10 m

# Heletz site parameters

| parameter | units | value | error |
|---|---|---|---|
| → temperature | °C | 66 | ± 1 |
| → pressure | MPa | 14.7 | ± 1 |
| salinity | %-mass | 0.055 | ± 0.005 |
| → porosity | % | 20 | ± 5 |
| → horizontal permeability | mD | 700 | ×/÷ 10 |
| vertical permeability | mD | 100 | ×/÷ 10 |
| rock grain density | kg/m³ | 2870 | ± 75 |
| rock bulk density | kg/m³ | 2300 | ± 300 |
| wet thermal conductivity | W/m/K | 4.0 | ± 0.8 |
| dry thermal conductivity | W/m/K | 2.6 | ± 0.6 |
| specific heat | J/kg/K | 920 | ± 100 |
| thickness of target horizon | m | 11, with 2 layers: 2 m + 9 m | ± 4 to 6 |

core samples

lab measurements

[Benson et al., 2013]

[Bensabat et al., 2013]

[Cermak + Rybach, 1992]

[Edlmann,2013]

[Niemi et al, 2014

[Pruess et al., 2012]

[Shtivelman, 2010]

[Vosteen + Schellschmidt, 2003]

| minerals (I) | | |
|---|---|---|
| primary minerals | volume fraction [%] | secondary minerals |
| **carbonates** | | |
| → ankerite e.g. $CaFe(CO_3)_2$ | 3.7 | calcite $CaCO_3$ |
| | | siderite $FeCO_3$ |
| **feldspar** | | |
| K-feldspar $KAlSi_3O_8$ | 12 | |
| albite $NaAlSi_3O_8$ | 2.5 | |
| **clay minerals** | | |
| illite e.g. $K_{0.85}Al_{2.85}Si_{3.15}O_{10}(OH)_2$ | 3.9 | |
| chlorite $(Mg,Fe)_3(Si,Al)_4O_{10}$ | 1.4 | |
| kaolinite $Al_2Si_2O_5(OH)_4$ | 3.2 | |

# Heletz site parameters

| minerals (II) | | | |
|---|---|---|---|
| primary minerals | | volume fraction [%] | secondary minerals |
| **sulfur minerals** | | | |
| → anhydrite | $CaSO_4$ | 0.4 | |
| → pyrite | $FeS_2$ | 2.1 | |
| **sandstone** | | | |
| quartz | $SiO_2$ | 69.3 | |
| **iron minerals** | | | |
| goethite | FeOOH | 1.5 | hematite $Fe_2O_3$ |

thermodynamic data – EQ3/6 database and [Wolery, 1992]

kinetic data – [Palandri and Kharaka, 2004]

[Zhang et al, 2011], [Xu et al., 2006]

## 1D model

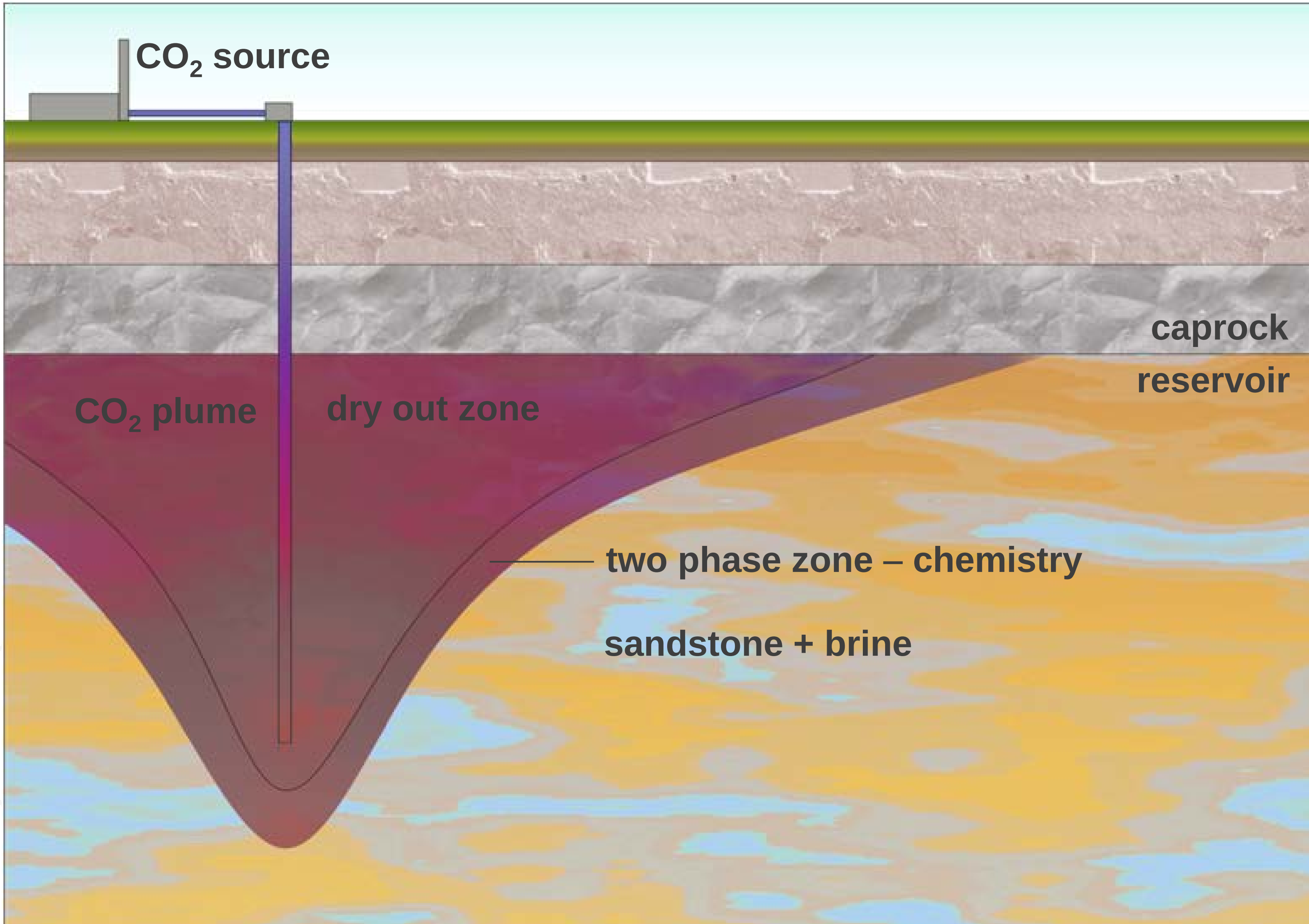
- radial symmetry
- injection of $CO_2$ with 1 % $SO_2$

## scope

- different time scales
- transport vs. aqueous chemistry
- mineral reaction

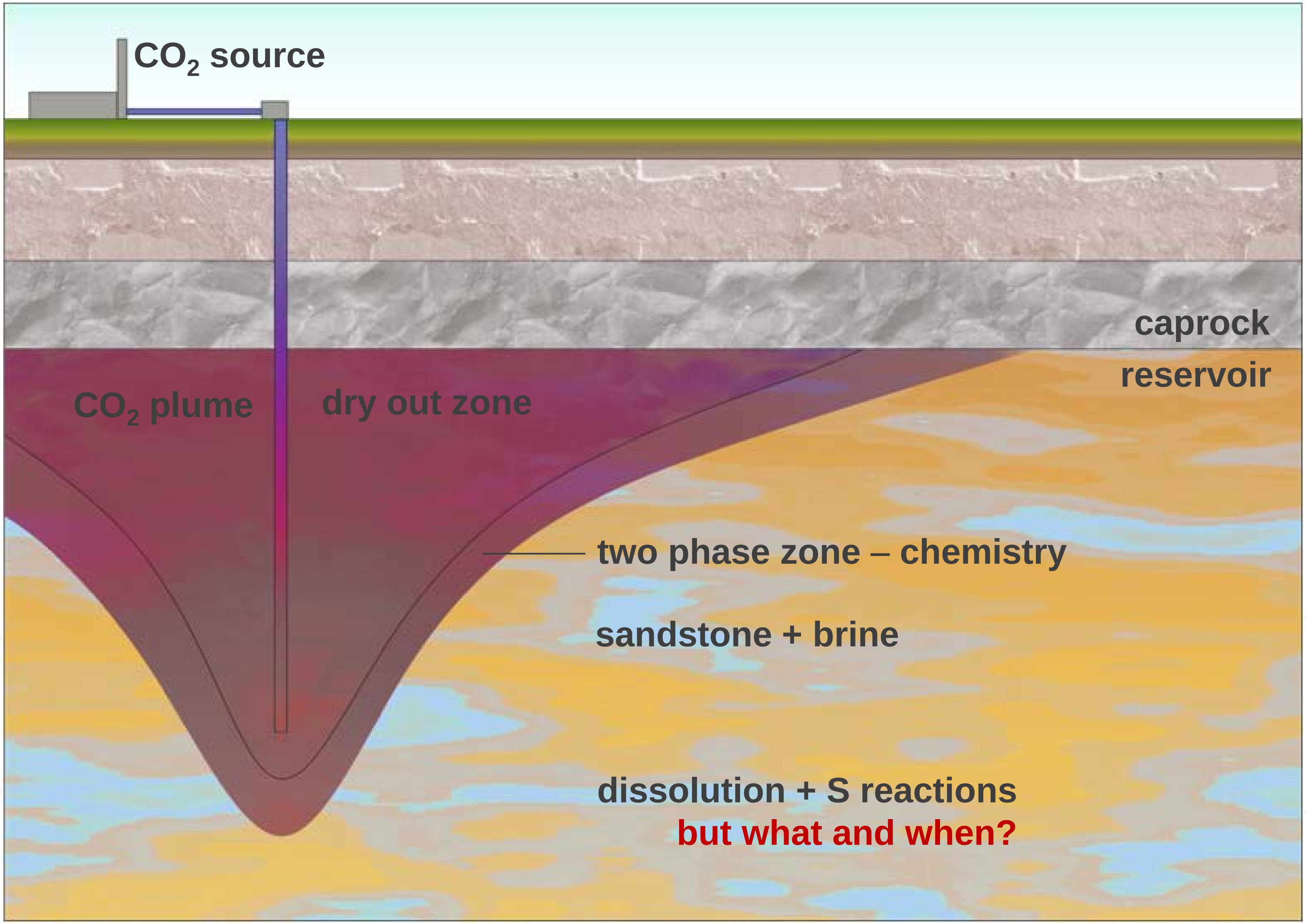
# reservoir

## area of interest

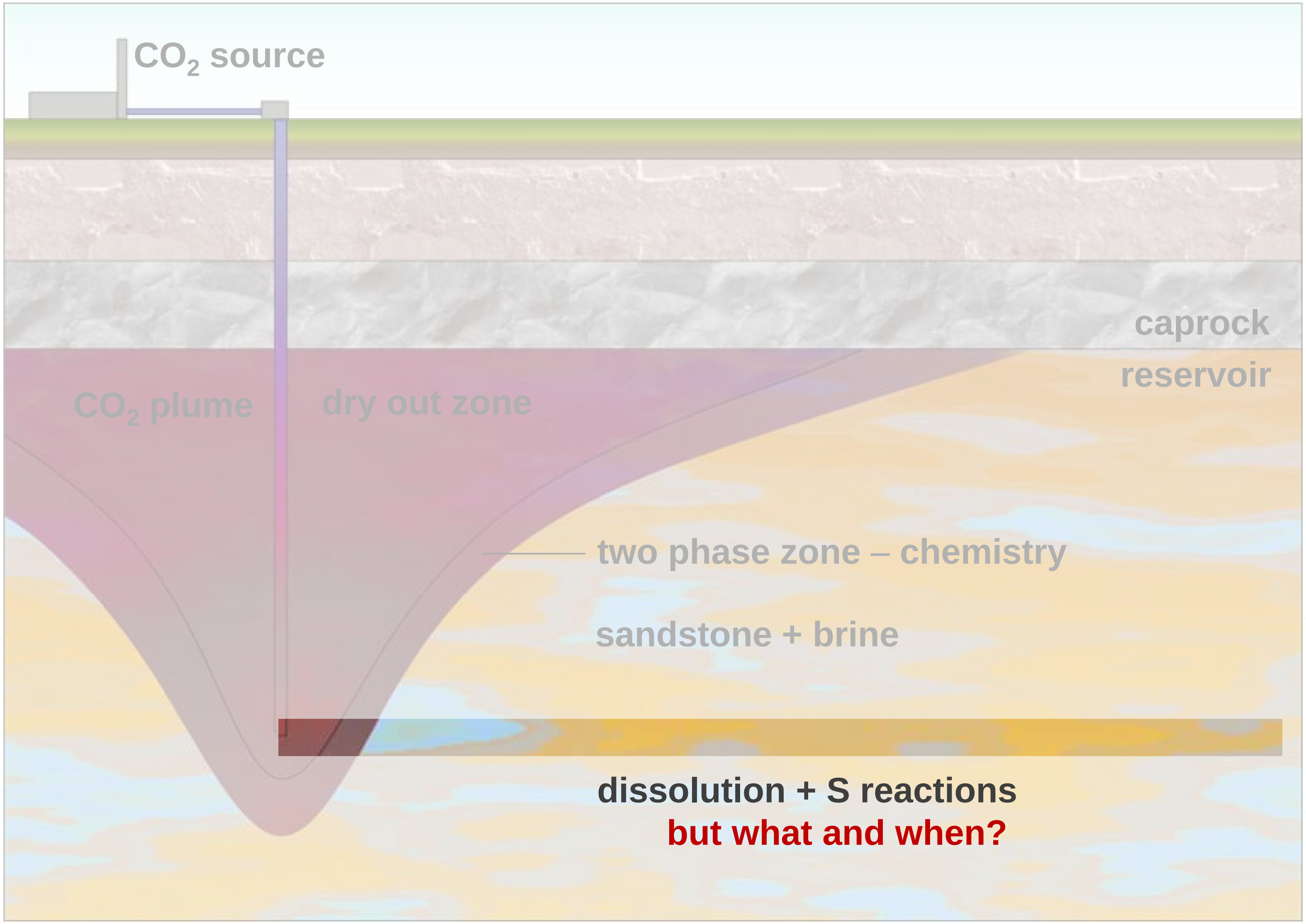


# reservoir

# area of interest



# area of interest



# 1D model setup

**1D model, radial**

– horizontal 30 km
  of chemical interest 100 m to 1500 m
– vertical 11 m

**cells**

– total 500
– cell size 0.112 m to 2545 m

**injection**

$CO_2$ with 1 % $SO_2$, 9.0 kg/s
simulation period 10 a

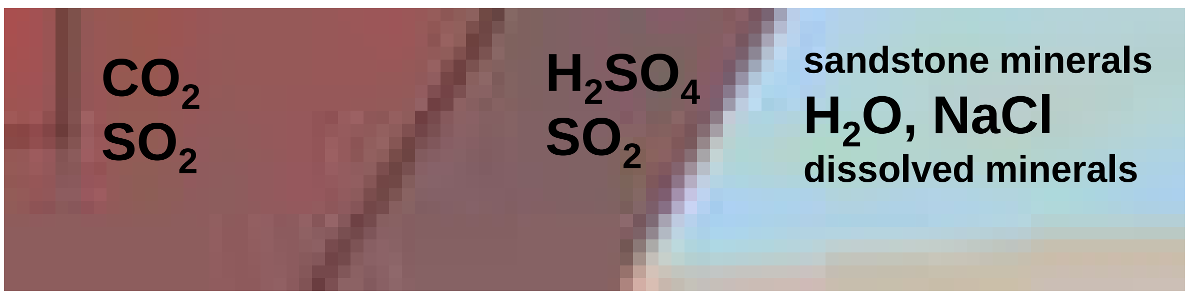
# 1D model

# reactive zones

# 1D model

# reactive zones

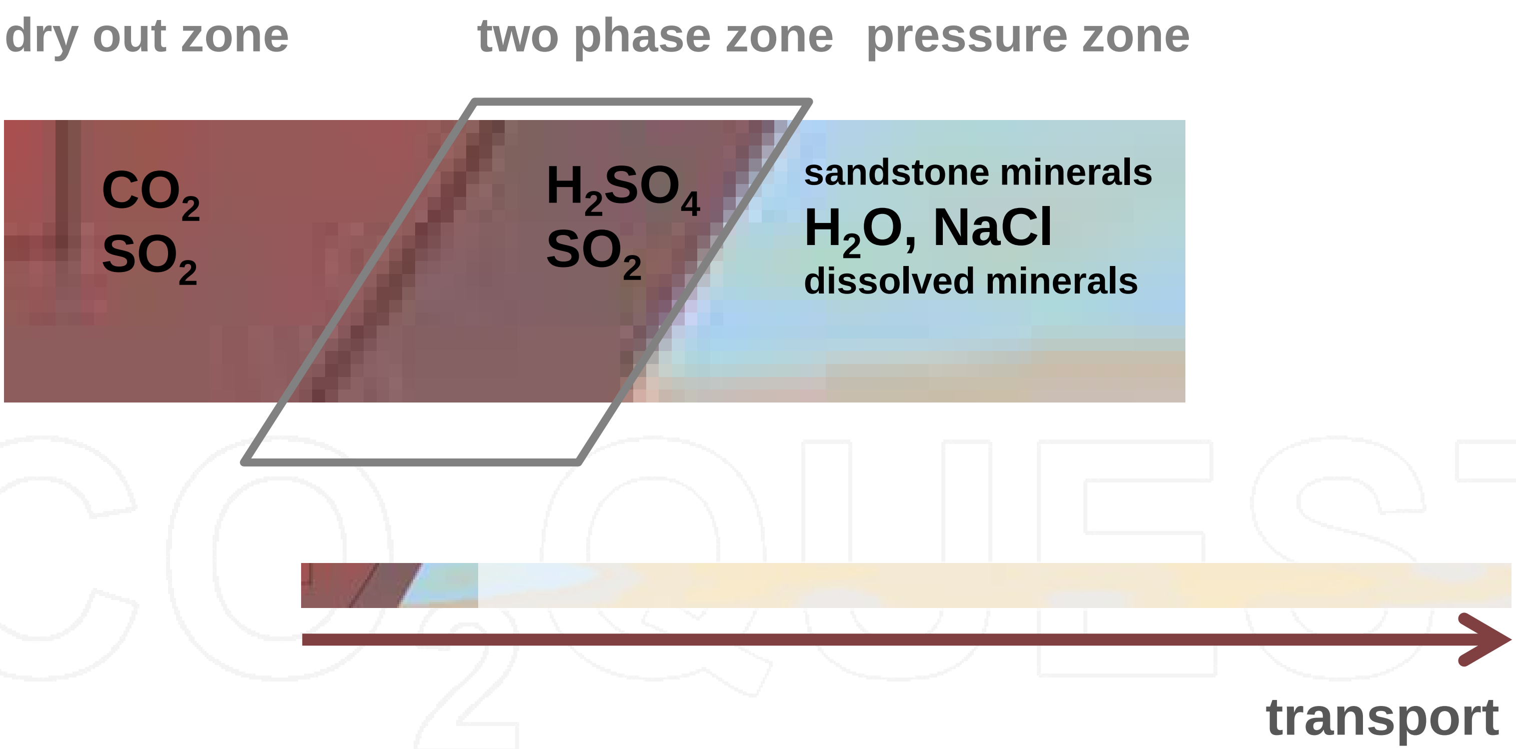
## chemically of interest




# 1D model

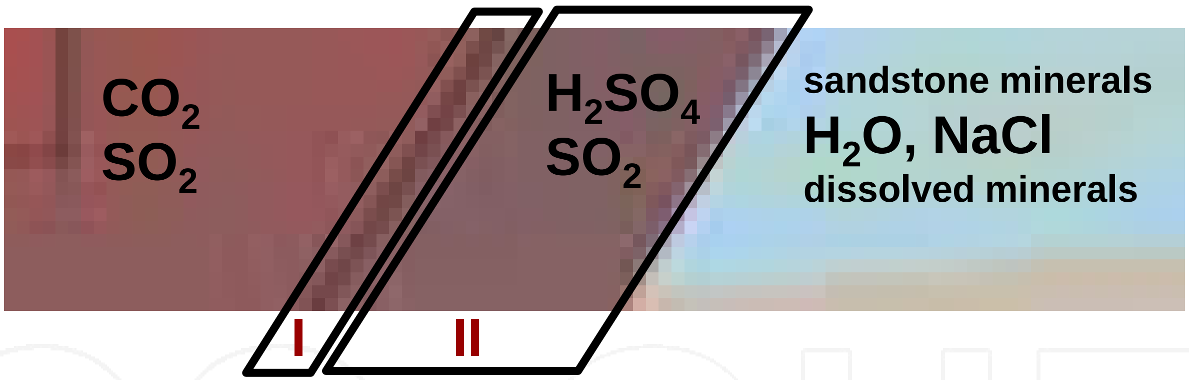
# reactive zones

## chemically of interest



# 1D model

# reactive zones




**in two phase zone distinguish reactive zones I and II**

**(I)**

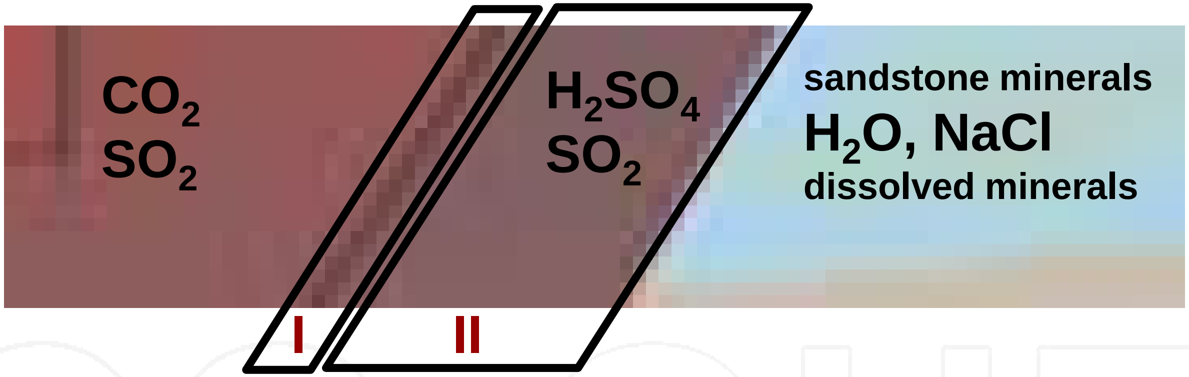
- closer to injection point
- high dissolution rate
- narrow zone

**(II)**

- farther away
- slow, only small chromatographic dissociation

→ $SO_2$ distribution in broad zone

- low concentration




# 1D model

# injection

## injection

**sc gas phase ($CO_2$)**
**$SO_2$(g)**

↓

**aqueous phase (brine)**
**$SO_2$(aq)**

↓

**$H_2SO_3$(aq)**
**$H_2S$(aq)**
**$H_2SO_4$(aq)**

# 1D model



injection

**sc gas phase ($CO_2$)**
**$SO_2$(g)**

↓ dissolution, fast

**aqueous phase (brine)**
**$SO_2$(aq)**

↓ conversion, slow?
hydrolysis, disproportion, oxidation

**$H_2SO_3$(aq)**
**$H_2S$(aq)**
**$H_2SO_4$(aq)**

reaction

# 1D model

## transport

injection

transport

**sc gas phase ($CO_2$)**
**$SO_2$(g)**

dissolution, fast

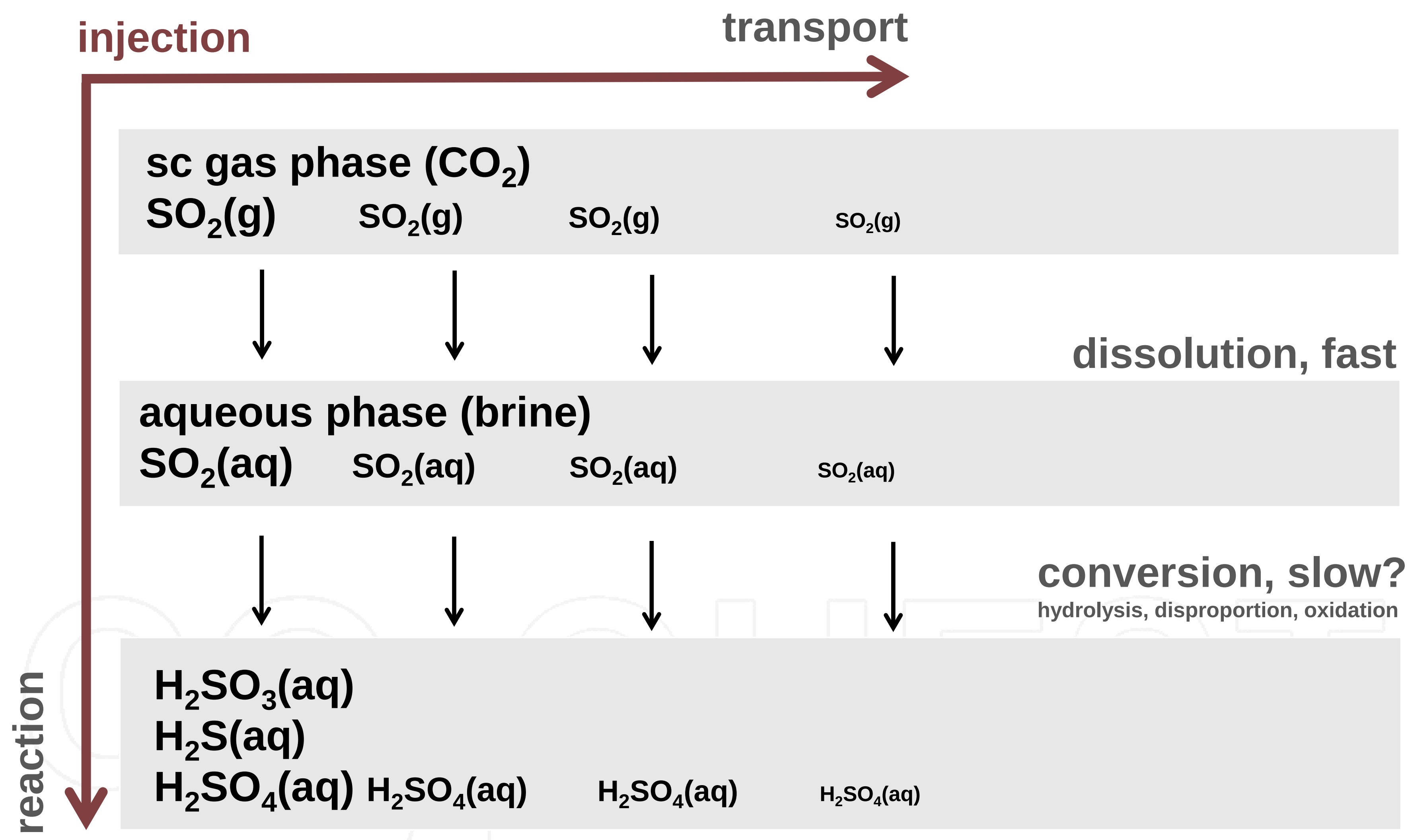
**aqueous phase (brine)**
**$SO_2$(aq)**

conversion, slow?
hydrolysis, disproportion, oxidation

**$H_2SO_3$(aq)**
**$H_2S$(aq)**
**$H_2SO_4$(aq)**

reaction

# 1D model transport



## $SO_2$ dissolution and oxidation

**main problem**

→ **chemical conversion rates of $SO_2$ under geological storage conditions are controversial and/or unknown**

## transport vs. $SO_2$ oxidation rate

$$r_{\text{transp}} = \frac{\mathrm{d}n}{\mathrm{d}t \cdot \mathrm{d}V_{\text{aq}}} = \frac{c_{\text{gas}} \cdot S_{\text{g}}}{\mathrm{d}t \cdot (1 - S_{\text{g}})}$$

0.02 mol·L$^{-1}$·s$^{-1}$ to 0.07 mol·L$^{-1}$·s$^{-1}$

$$r_{\text{oxidation}} = k_{(\text{T}=66°C,\, p=14.7\,MPa)} \cdot a(SO_{2(aq)})$$

$10^{-10}$ mol·L$^{-1}$·s$^{-1}$ to $10^{-1}$ mol·L$^{-1}$·s$^{-1}$

**rate studies at atmospheric conditions — but geological conditions**

**higher temperature → increase of reaction rate**

**higher salinity → decrease of reaction rate**

**equilibrium speciation – infinitely fast conversion**

**kinetically delayed speciation – slow conversion**

**applied value for oxidation: 5·10$^{-7}$ mol·L$^{-1}$·s$^{-1}$**

# Transport Of Unsaturated Groundwater + Heat

**THMC numerical simulation**
**multi-dimensional**
**coupled transport of water, vapor, non-condensible gas, and heat**
**porous and fractured media**
**LBNL Berkeley**
**finite differences**

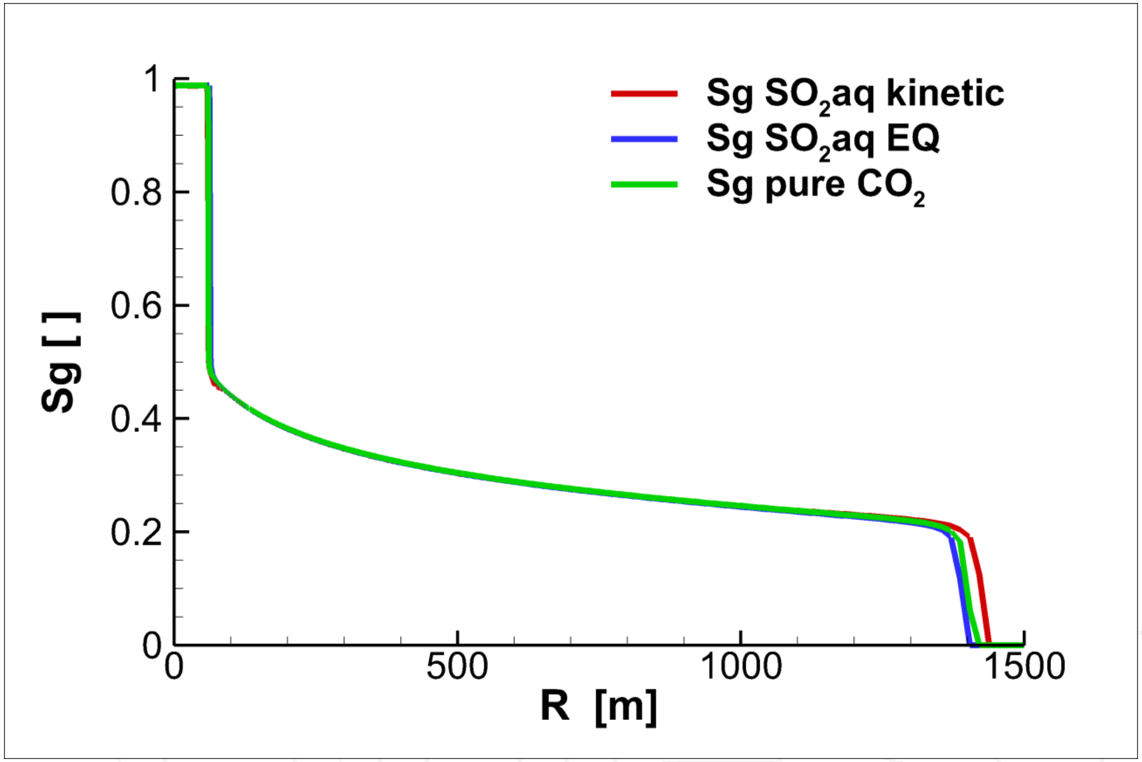
→ **injection of dissolved $SO_2$ in gas phase**
**TOUGHREACT 3.0-OMP + ECO2N**
**simulation of multiphase flow of pure gases**

## gas saturation

**compare pure $CO_2$ with $CO_2$+ $SO_2$ kinetic and equilibrium**

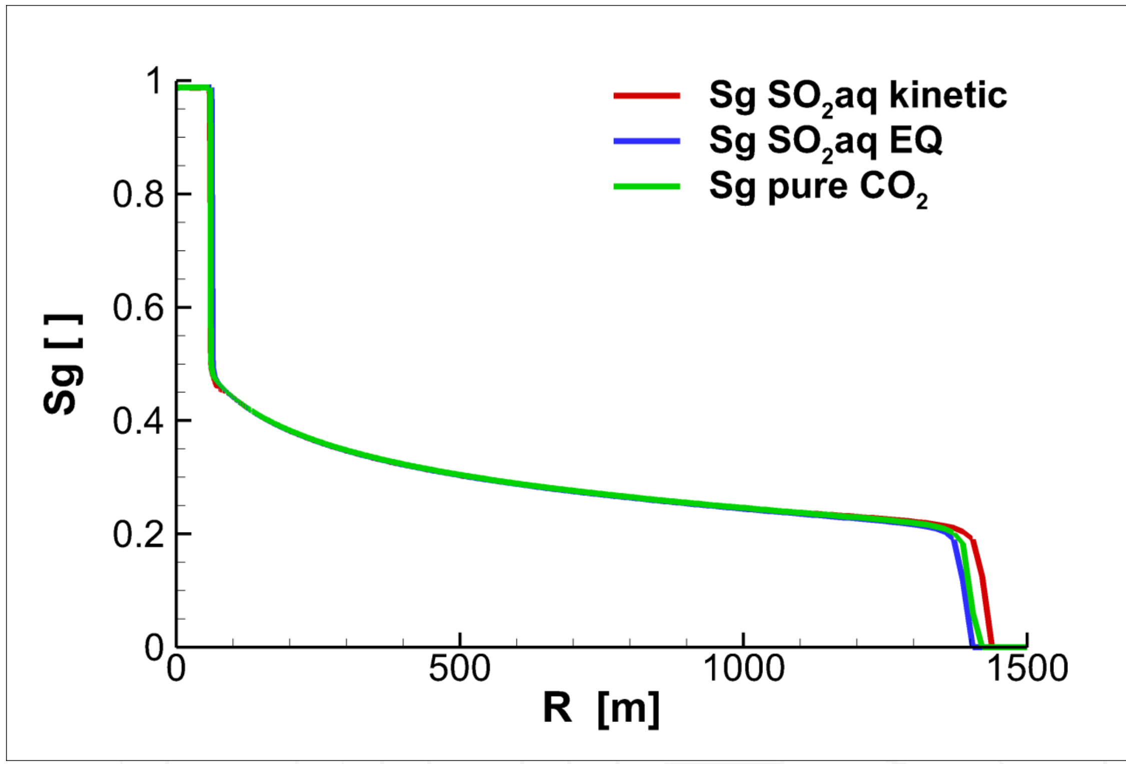
**no difference**

t = 10 a



## gas saturation

t = 10 a




**no difference**

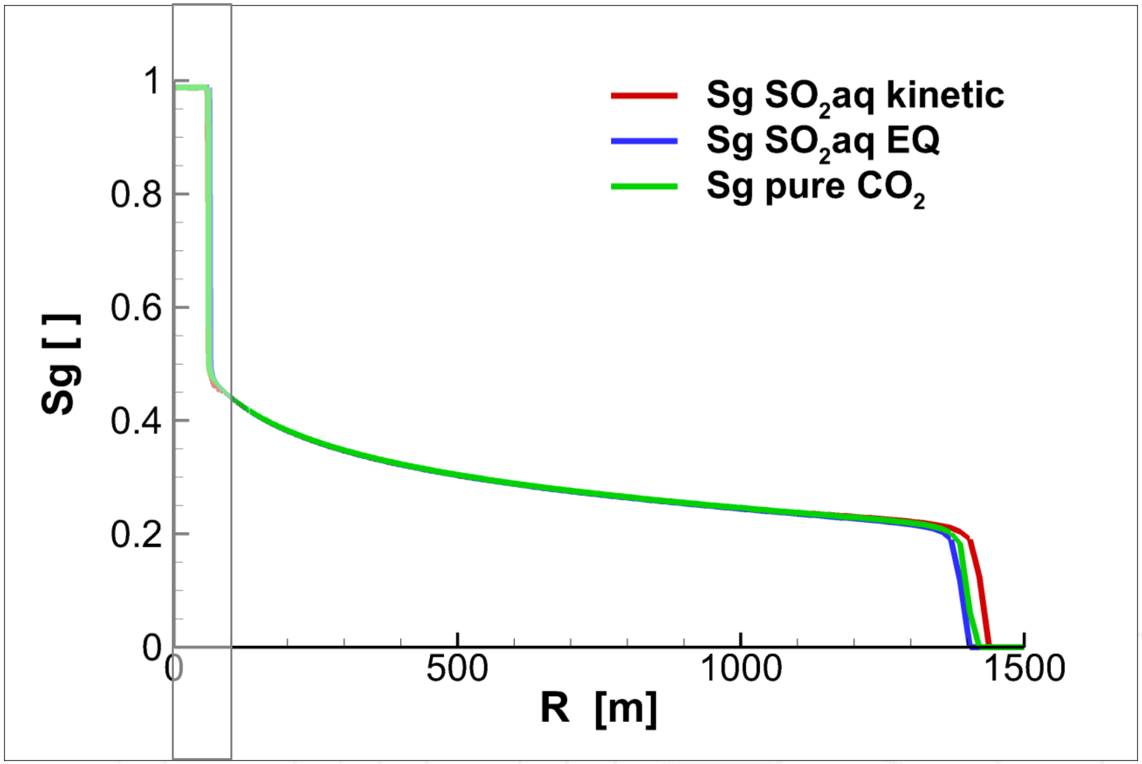
dry out zone → two phase zone pressure zone

< 100 m > 100 m > 1400 m

# Sg [0 m to 1500 m]

## gas saturation

t = 10 a

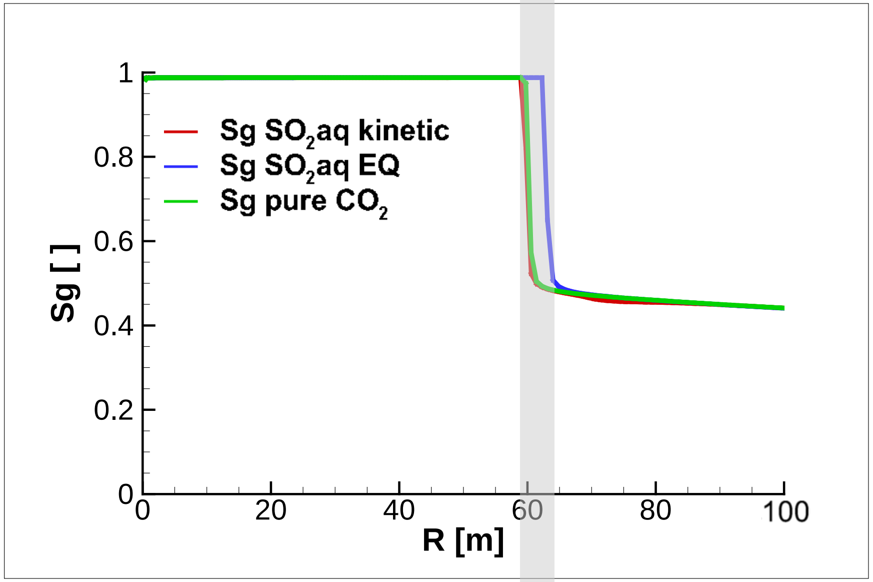



**no difference**

# results

# Sg [0 m to 100 m]

## saturation



# results

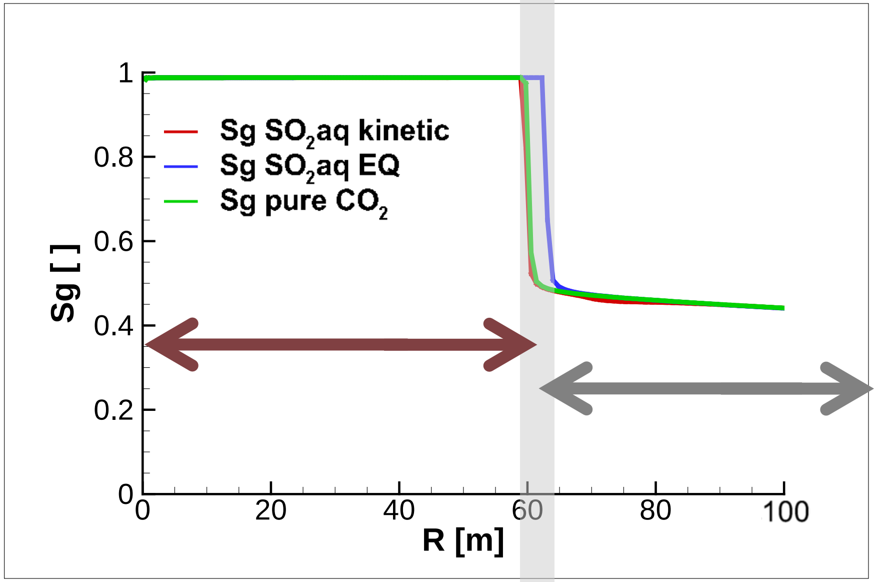


**saturation**

**in the presence of water**

**→ all $SO_2$ dissolves**

**delay of EQ compared to kinetic**




dry out zone

two phase flow zone

# results

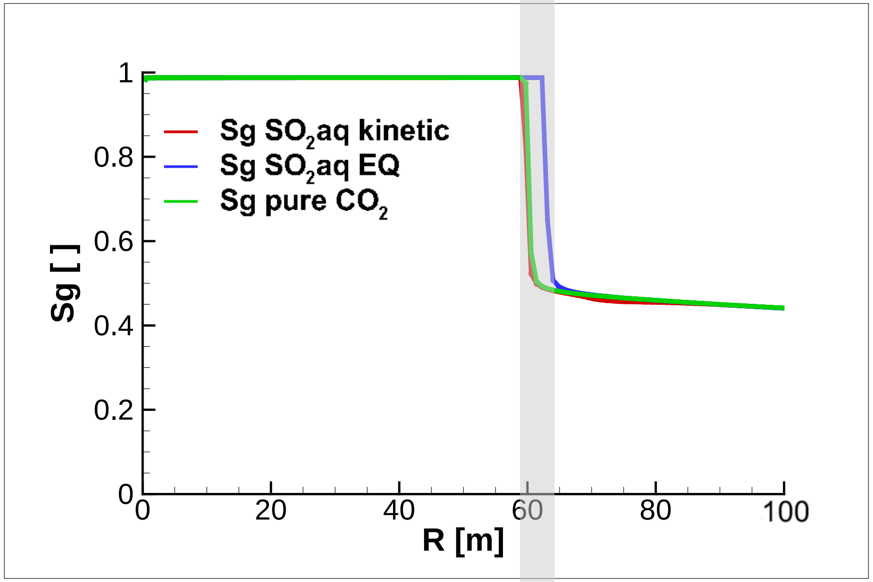
# $Sg$, $SO_2g$

**saturation**

**in the presence of water**

**→ all $SO_2$ dissolves**

**delay of EQ compared to kinetic**

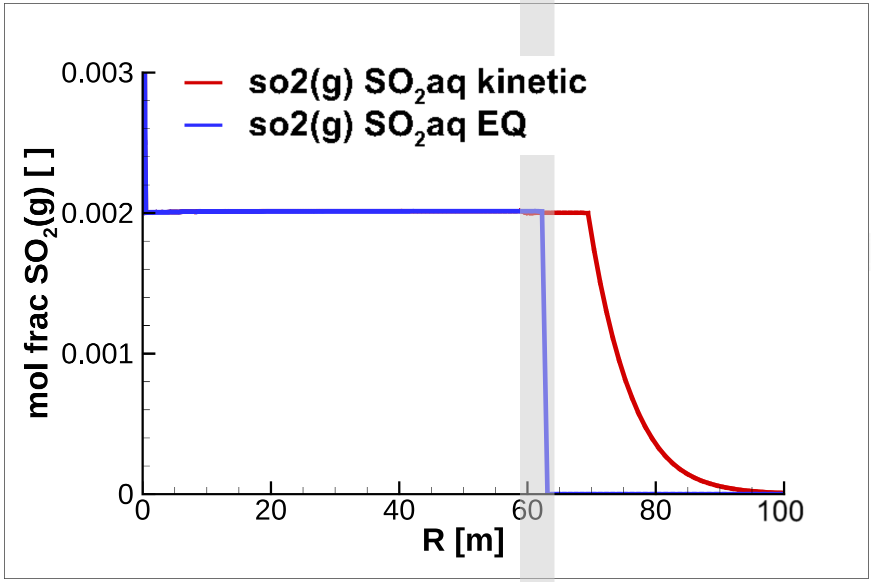



**$SO_2$ in gas phase**

**EQ – contact of water**

**→ all $SO_2$ dissolves**

**kinetic – delay of $SO_2$ dissolution**



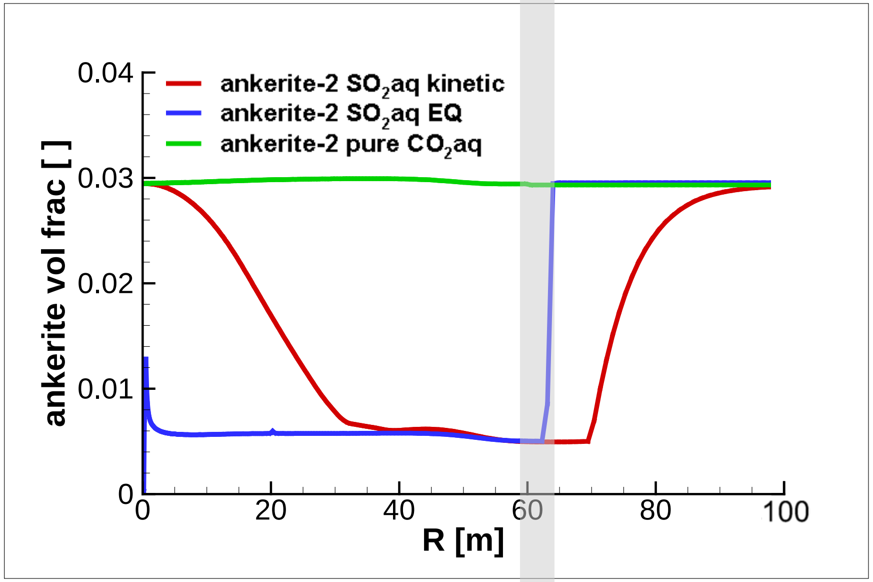
# results

# $CaFe[CO_3]_2$

**ankerite $CaFe[CO_3]_2$**

**EQ – difference to pure $CO_2$ til 60 m**

**kinetic – compared to EQ, first smaller dissolution due shorter residence time**
**→ diff. to pure $CO_2$ til 90 m**



# results

# $CaFe[CO_3]_2$, $CaCO_3$

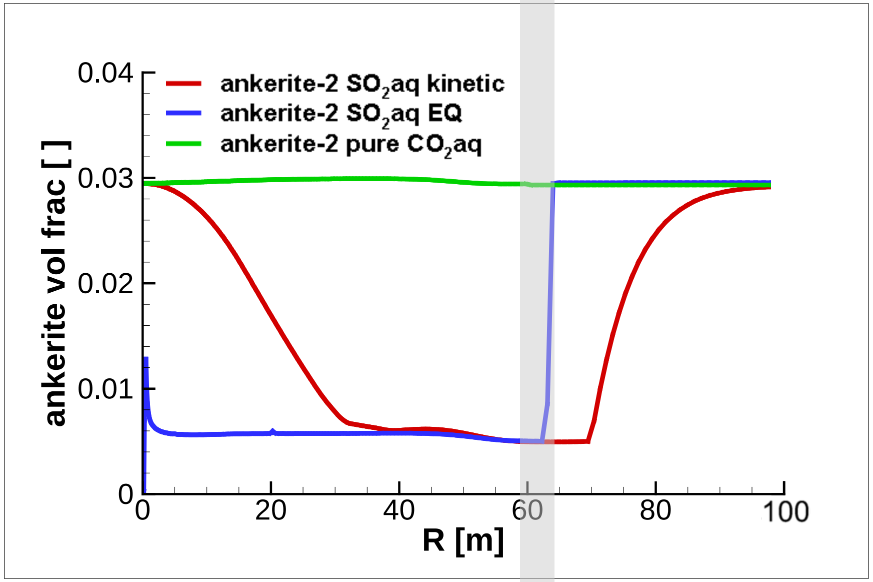
**ankerite $CaFe[CO_3]_2$**

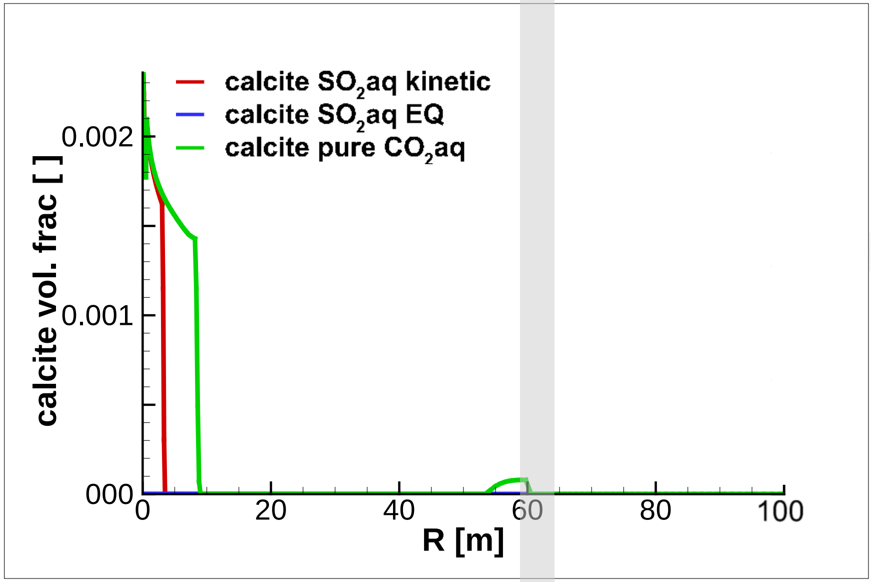
**EQ – difference to pure $CO_2$ til 60 m**

**kinetic – compared to EQ, first smaller dissolution due shorter residence time**
**→ diff. to pure $CO_2$ til 90 m**

**calcite $CaCO_3$**

**practically negligible**



# results

# $CaFe[CO_3]_2$, $FeCO_3$

**ankerite $CaFe[CO_3]_2$**

EQ – difference to pure $CO_2$ til 60 m

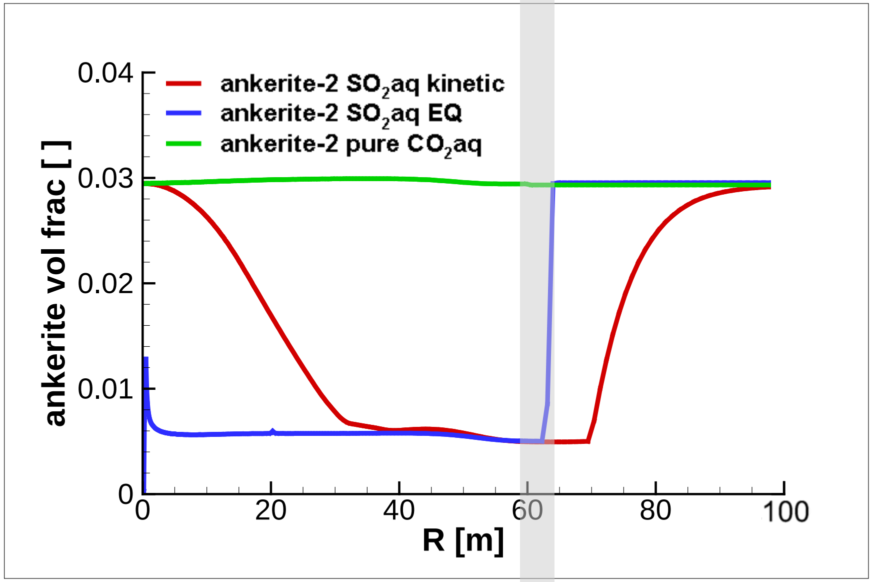
kinetic – compared to EQ, first smaller dissolution due shorter residence time
→ diff. to pure $CO_2$ til 90 m

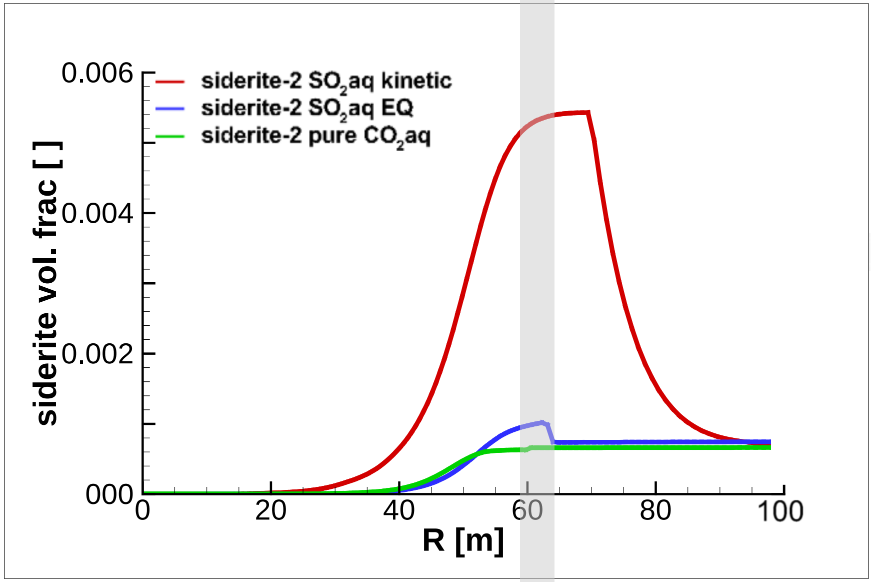
**siderite $FeCO_3$**

further away, small precipitation using Fe released by ankerite

EQ – precipitation similar to pure $CO_2$ case

kinetic – higher precipitation



# results

# $CaFe[CO_3]_2$, $CaSO_4$

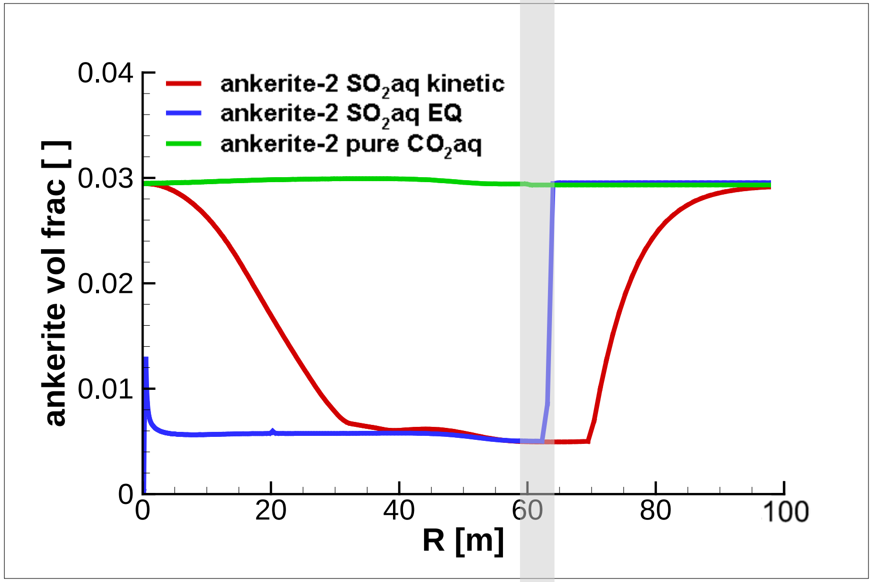
**ankerite $CaFe[CO_3]_2$**

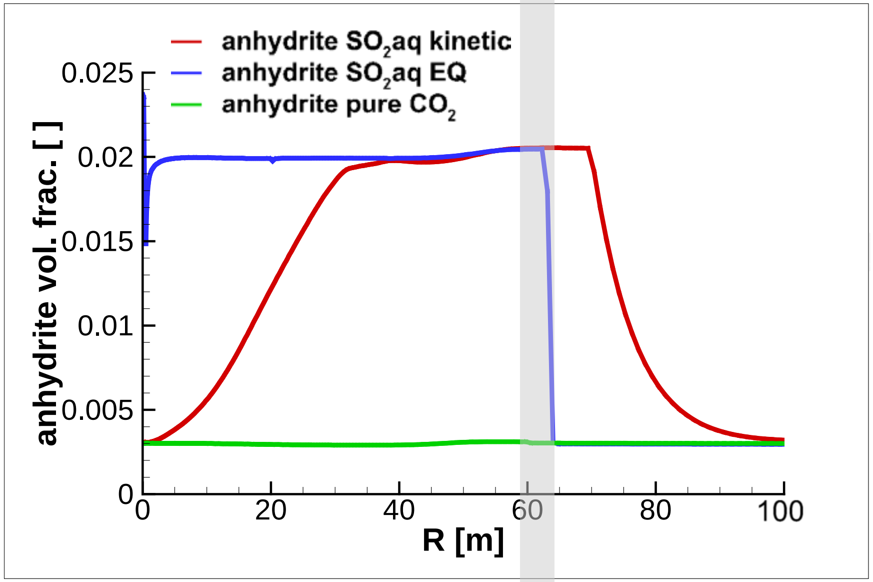
**EQ – difference to pure $CO_2$ til 60 m**

**kinetic – compared to EQ, first smaller dissolution due shorter residence time → diff. to pure $CO_2$ til 90 m**

**anhydrite $CaSO_4$**

- **free $Ca^{2+}$ from ankerite $CaFe[CO_3]_2$ precipitates as $CaSO_4$**
- **delay in kinetic simulation compared to EQ**



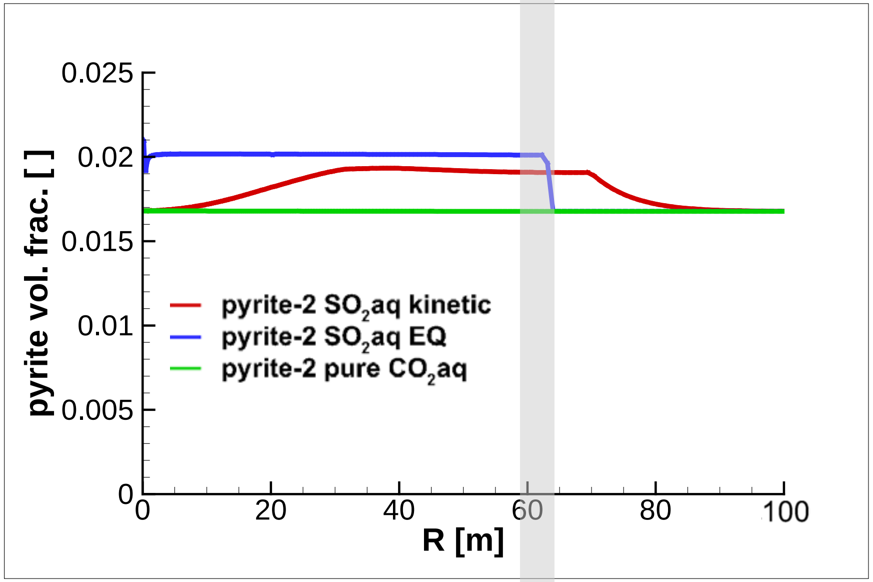



# results

## $FeS_2$, $CaSO_4$

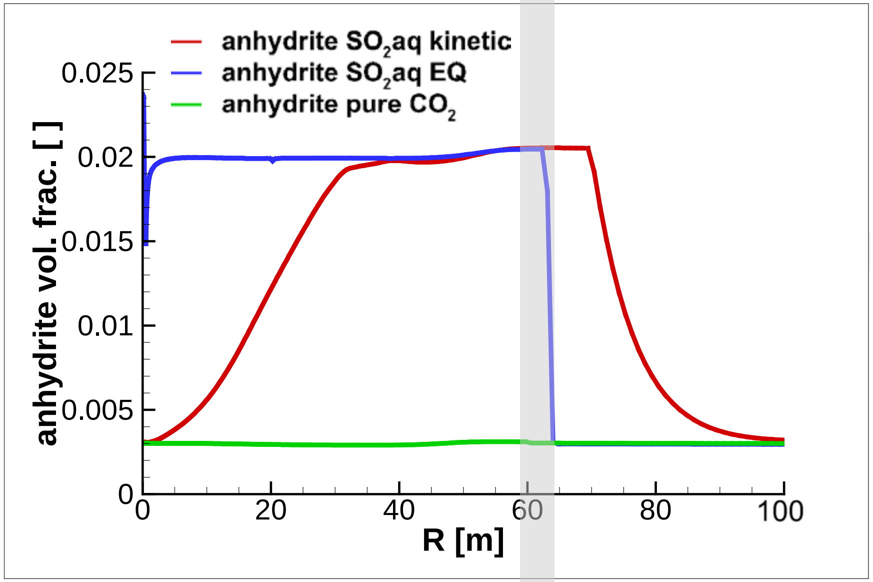
**pyrite $FeS_2$**

- precipitates parallel to anhydrite
- Fe from ankerite




**anhydrite $CaSO_4$**

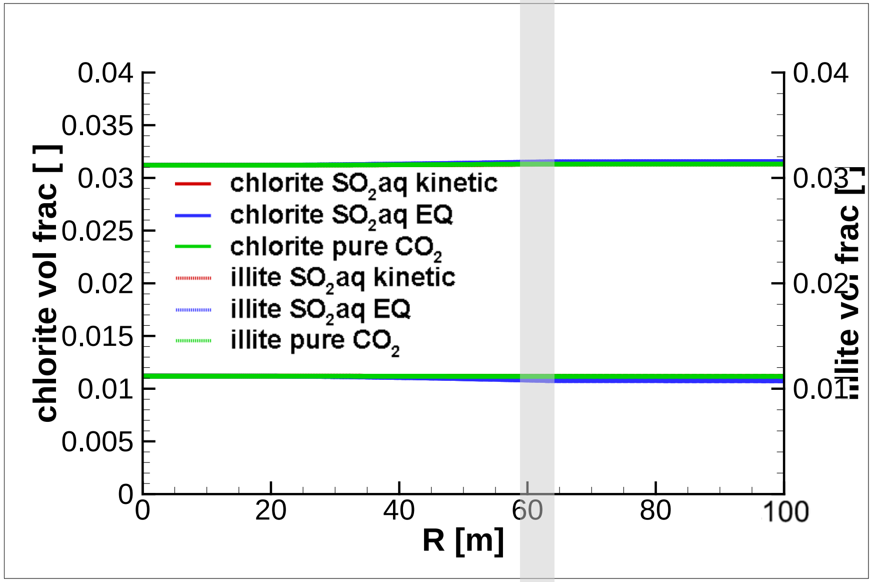
- free $Ca^{2+}$ from ankerite $CaFe[CO_3]_2$ precipitates as $CaSO_4$
- delay in kinetic simulation compared to EQ



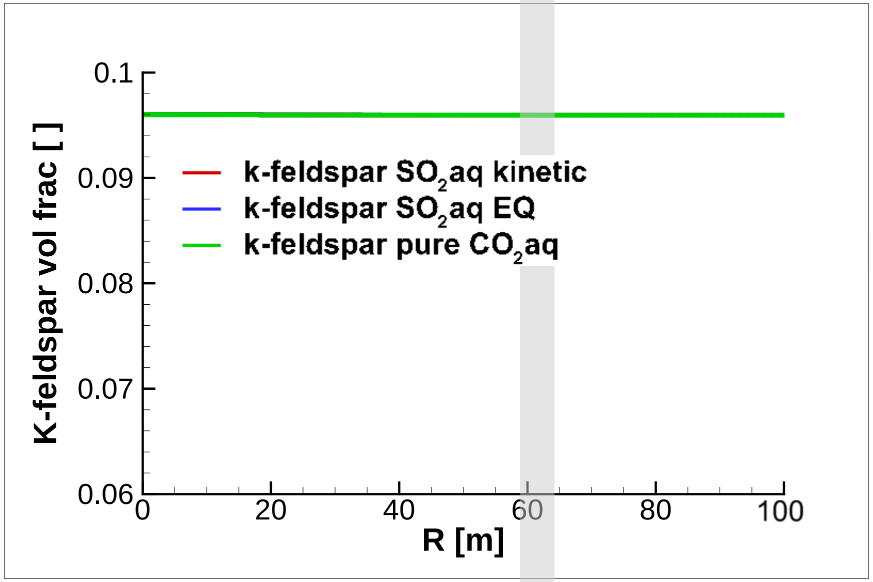
# results

# clays

**clorite, $(Mg,Fe)_3(Si,Al)_4O_{10}$**
**illite, e.g. $K_{0.85}Al_{2.85}Si_{3.15}O_{10}(OH)_2$**
– no changes




**K-feldspar, $KAlSi_3O_8$**
– no changes



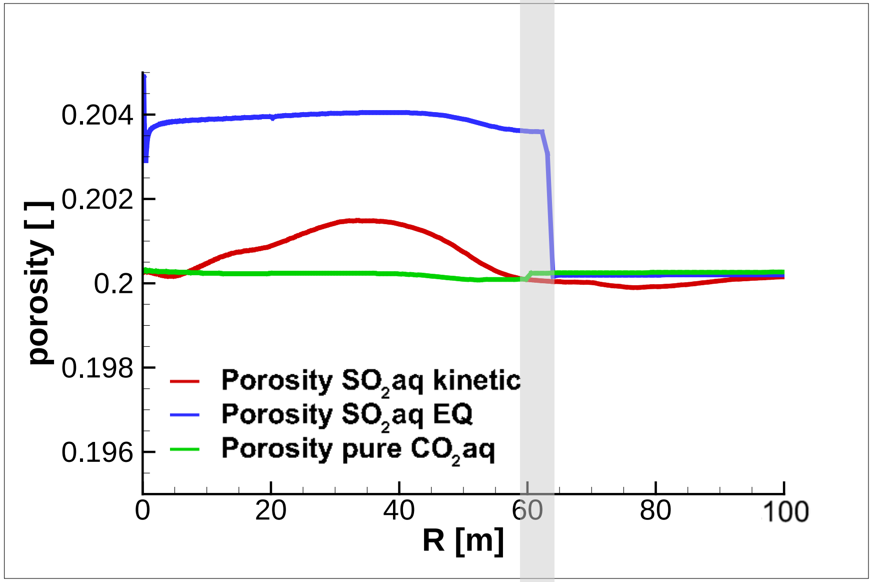
# results

# porosity

## porosity

– determined through Ca : $CO_3$, i.e. 1 : 2 as ankerite $CaFe[CO_3]_2$ more ankerite dissolves than anhydrite $CaSO_4$ precipitates

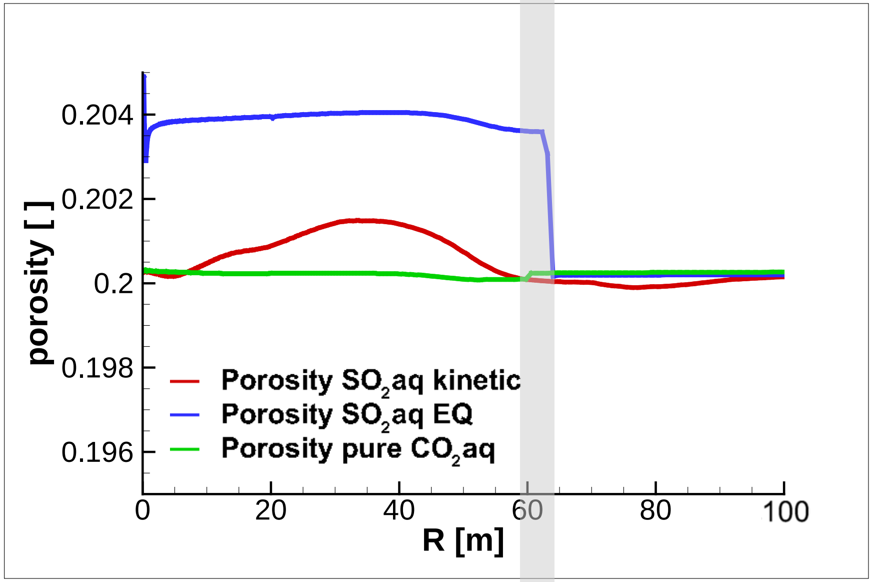
→ increase in porosity



# porosity

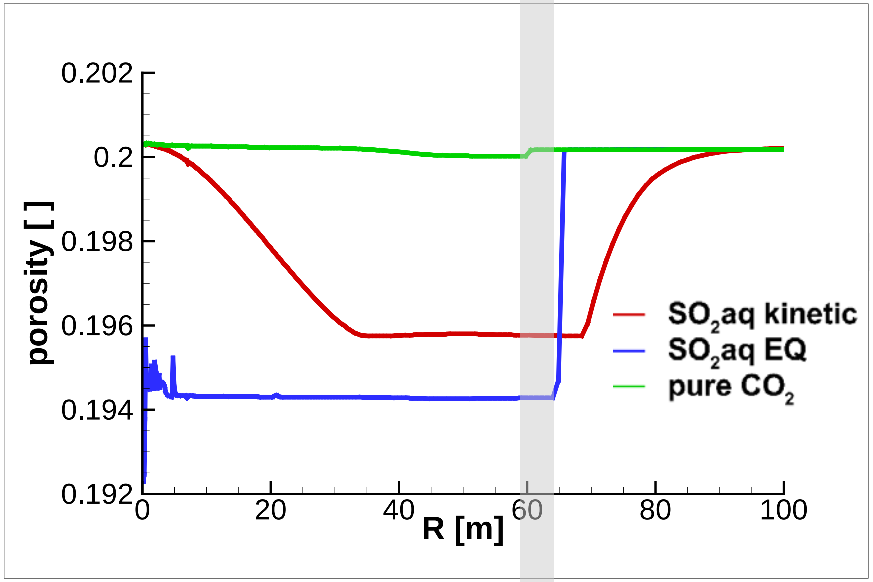
## porosity I

– determined through Ca : $CO_3$, i.e. 1 : 2 as ankerite $CaFe[CO_3]_2$ more ankerite dissolves than anhydrite $CaSO_4$ precipitates
→ increase in porosity




## porosity II

– with initial carbonate as calcite, i.e. Ca : $CO_3$ as 1 : 1
→ decrease in porosity as anhydrite has larger mole volume compared to calcite



# conclusions

$SO_2$ rather small impact

results dependent on
- real reservoir conditions,
  esp. carbonates and porosity
- chosen model
  kinetics versus equilibrium conditions

choose your models wisely

# outlook

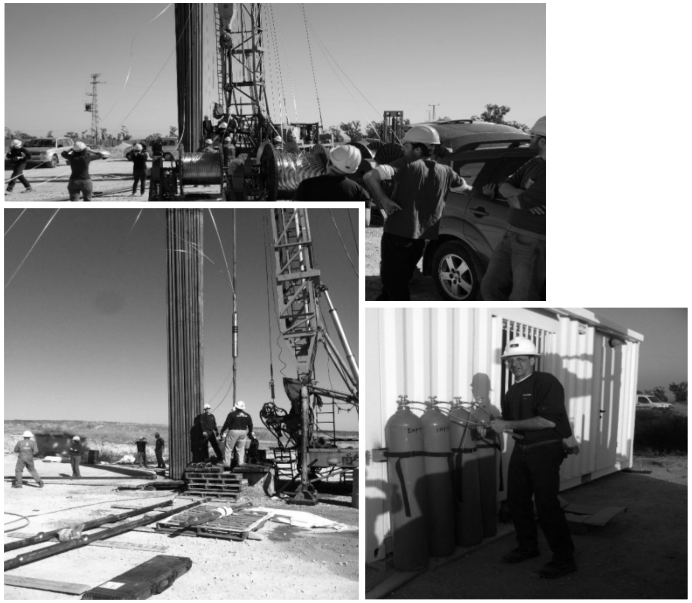
## outlook

**further model validation with Heletz data**

**further sensitivity analysis**

**influence of other impurities**

**1D → 2D reservoir model**



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# disclaimer

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## thank you