Oil Degradation in the Gullfaks Field (Norway): How Hydrogeochemical Modeling can Help to Decipher Organic-Inorganic Interactions Controlling CO_2 Fate and Behavior*

Wolfgang van Berk[1], Yunjiao Fu[2], and Hans-Martin Schulz[3]

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Abstract

Oil degradation in the Gullfaks Oilfield led to hydrogeochemical processes that caused (1) intense in-situ gas formation resulting in high CH_4 and CO_2 partial pressures, (2) an intense reservoir rock matrix alteration, and (3) a massive release of carbonate carbon and sodium into the formation water. We aim to quantitatively analyze the pathways of the complex, interconnected reactions and to retrace the consequences of these reactions by applying hydrogeochemical modeling. Our approach considers interactions among mineral assemblages (anorthite, albite, K-feldspar, quartz, kaolinite, goethite, calcite, dolomite, siderite, dawsonite, and nahcolite), aqueous solutions, and a multi-component fixed pressure gas phase (CO_2, CH_4, H_2). The modeling concept is based on the anoxic degradation of crude oil (irreversible conversion of n-alkanes to CO_2, CH_4, H_2, and acetic acid) at oil-water contacts. These water-soluble degradation products are the driving forces for inorganic reactions to finally reaching equilibrium conditions. By using the USGS's computer code PHREEQC, the modeling results quantitatively reproduce the proven reservoir rock matrix alteration triggered by oil degradation showing: (1) a nearly complete dissolution of plagioclase, (2) the stability of K-feldspar, (3) a massive formation of kaolinite, and to a lesser degree of Ca-Mg-Fe carbonate, as well as (4) an observed unusually high CO_2 partial pressure (61 psi at maximum). In addition, this modeling reveals a specific sequence of alteration reactions which are coupled to the release of CO_2. The evolving composition of co-existing formation water is strongly influenced by the uptake of carbonate carbon from oil degradation and sodium released from dissolving albitic plagioclase. Nahcolite ($NaHCO_3$; instead of thermodynamically stable dawsonite) forms as a CO_2 sequestering sodium carbonate, likely controlling CO_2 partial pressure. High degrees of modeled oil degradation, resulting rock matrix alteration and nahcolite formation lead to CO_2 and CH_4 partial pressures similar to those observed in the areas of the Gullfaks Field with strong degradation. The illustrated and quantitatively retraced diagenetic features can be taken as proxies for intense oil degradation; the degree of oil degradation and the described coupled inorganic processes including potential nahcolite formation are key factors affecting the amount and composition of gas generated in the Gullfaks oil reservoir.

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AAPG ACE / 6 – 9 April / Houston

Theme 7: Biodegradation and Alteration, Biogenic Gas (1)

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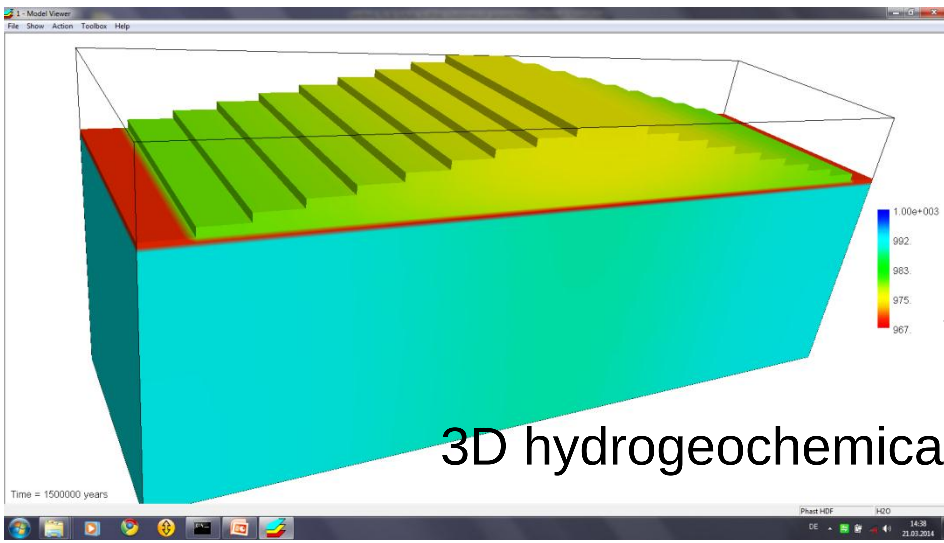

Water In Petroleum Systems

3D hydrogeochemical reactive mass transport modeling

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Clausthal University of Technology

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Potsdam

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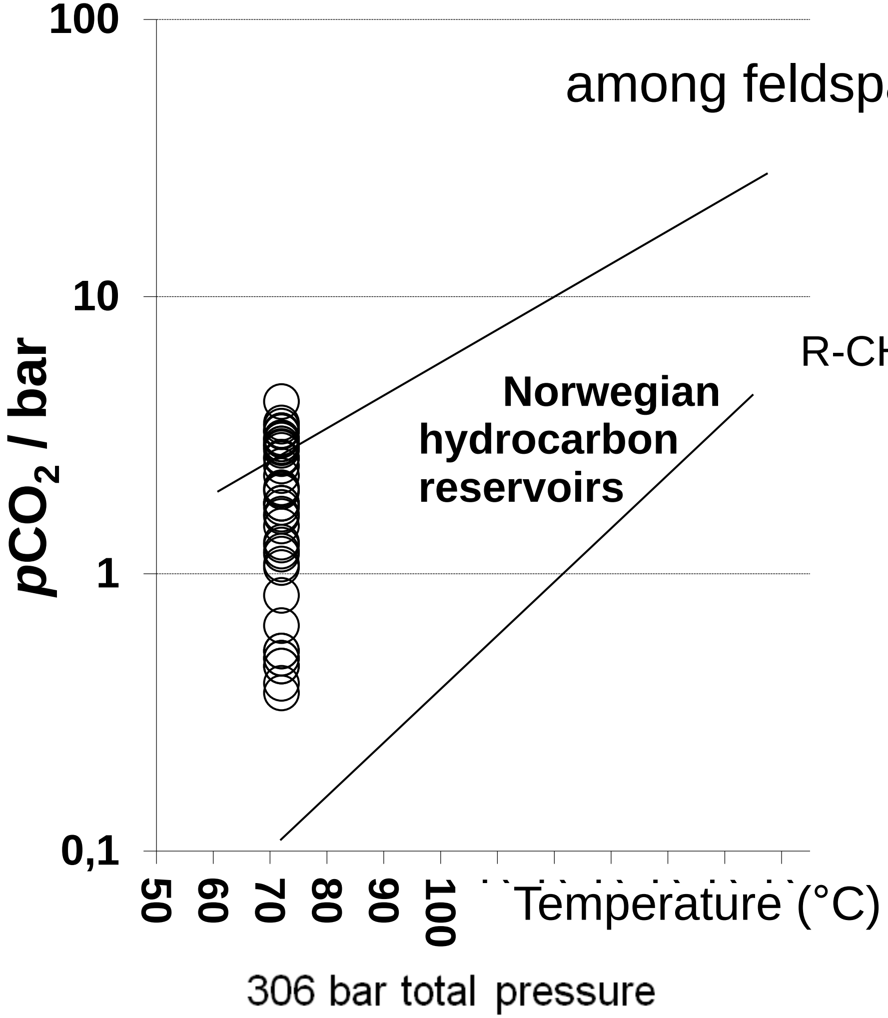
interpretation:
chemical equilibrium reactions
among feldspars, kaolinite, quartz, and carbonates
in the pore water

triggered by oil degradation

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

Smith & Ehrenberg (1989)

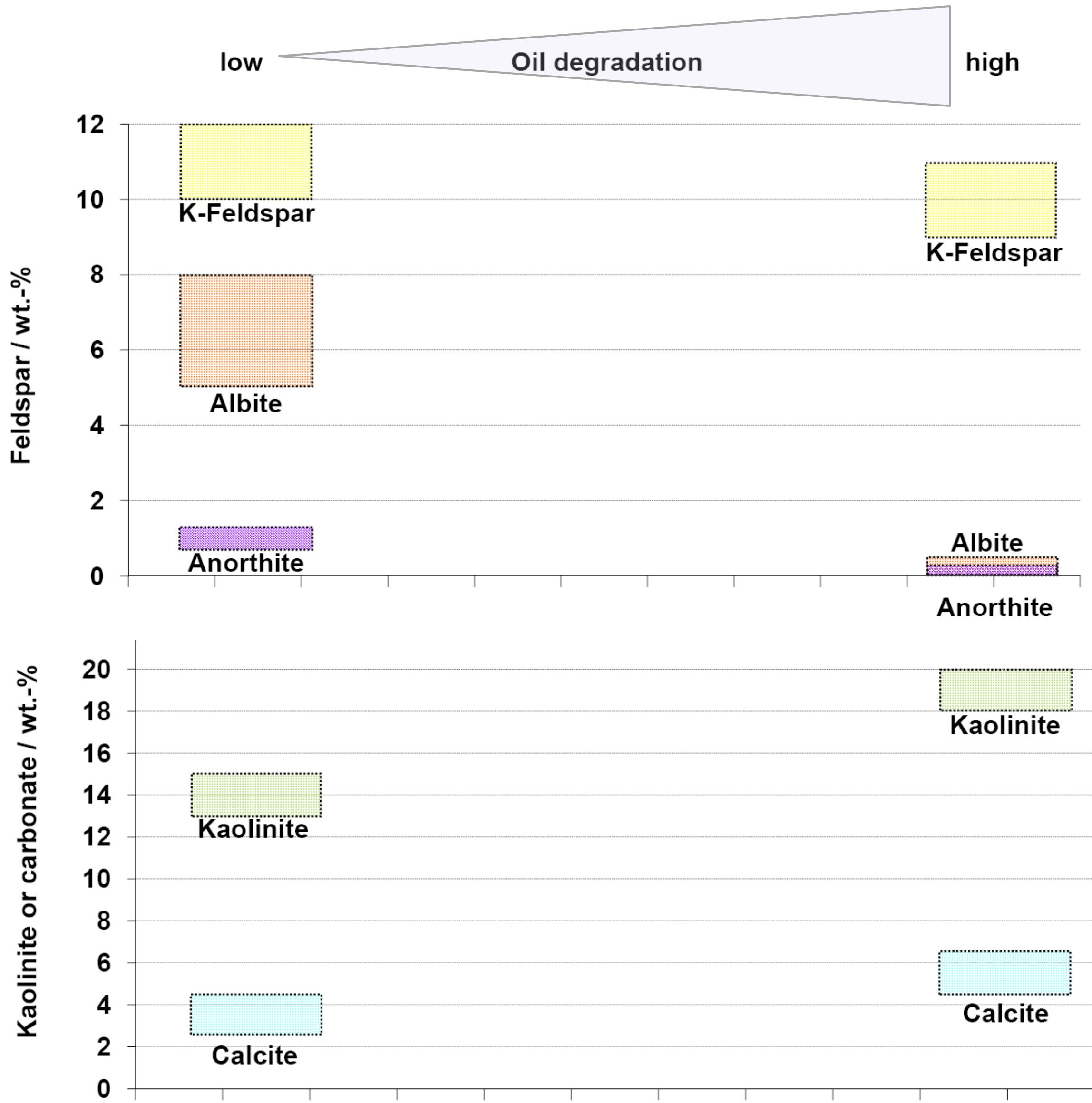


Smith & Ehrenberg (1989)

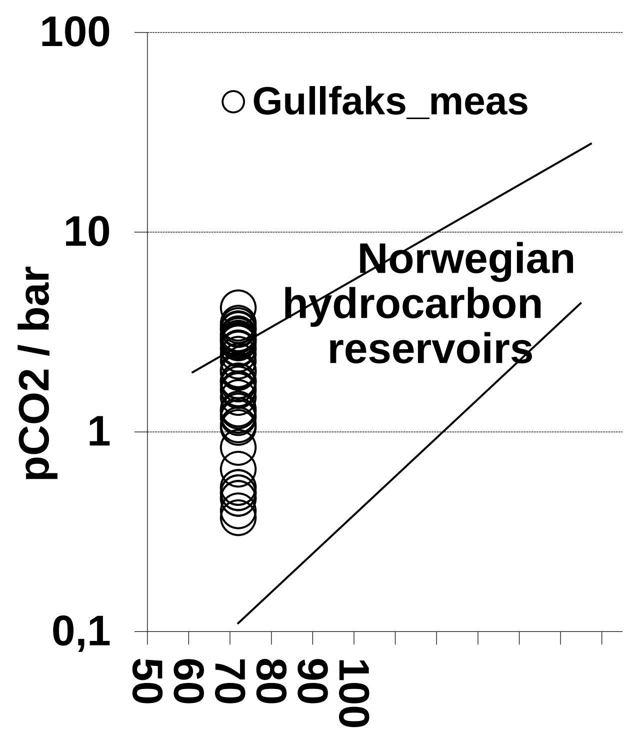
Gullfaks / Brent sandstone / observations / proxies indicating oil degradation (3)

N **S**

Horstad et al., 1992: degree of oil degradation > 10%

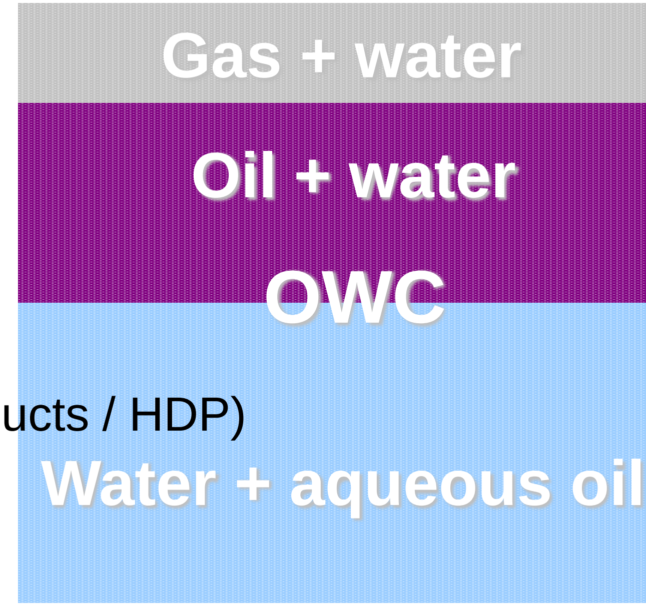


measured data from
Ehrenberg & Jakobsen (2001)



Smith & Ehrenberg (1989)

Water in petroleum systems / anoxic oil degradation (4)



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

(**H**ydrocarbon**D**egradation**P**roducts / HDP)

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + \mathbf{4H_2O} \rightarrow R + 1.9CO_2 + 0.1CH_3COOH + 0.9CH_4 + 5H_2$$

(Seewald, 2003)

hydrolytic redox reaction (disproportionation) of light paraffins

(Helgeson et al., 1993; Seewald, 2003)

kinetically controlled irreversible reactions

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

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 4H_2O \rightarrow R + 1.9CO_2 + 0.1CH_3COOH + 0.9CH_4 + 5H_2$$

CO_2 partial pressure / mol% $CO_{2(g)}$ in a multi-component gas

$CaAl_2Si_2O_6$ / $NaAlSi_3O_8$ / $KAlSi_3O_8$

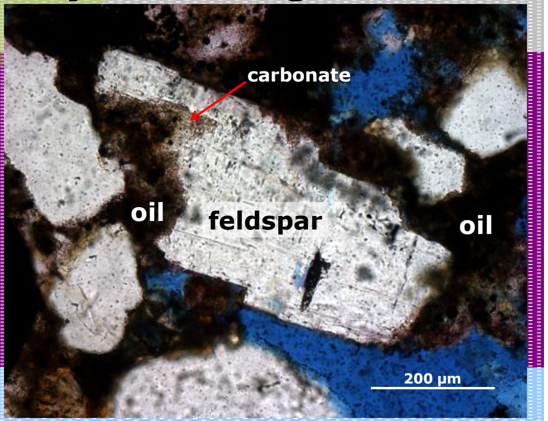
kaolinte / quartz / calcite

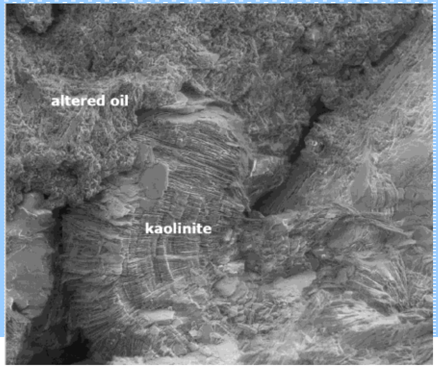
OWC

FeOOH

siderite/dolomite/nahcolite

$CO_{2(aq)}/CO_{2(g)}$ $CH_{4(aq)}/CH_{4(g)}$ $H_{2(aq)}/H_{2(g)}$





conceptual model / „0D“ (batch) reactor / modeling tool (6)

Ehrenberg & Jacobsen (2001): "… acid components from biodegradation selectively reacted with albitic plagioclase to form **kaolin**, releasing sodium bicarbonate into the residual water".

$$2CO_2 + \mathbf{2NaAlSi_3O_8} + 3H_2O = Al_2Si_2O_5(OH)_4 + 4SiO_2 + 2Na^+ + 2HCO_3^-$$

v_{tot} = 5 L **72°C / 310 bar** **p_V = 1 L**

6.4 mol *n*-alkane $C_{10}H_{22}$

Oil Reactor

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

$$\mathbf{\rightarrow R + 1.9CO_2 + 0.1CH_3COOH + 0.9CH_4 + 5H_2}$$

10.6 kg quartz, anorthite, **albite**, adularia, **kaolinite**, calcite, goethite siderite, dolomite, nahcolite / $NaHCO_{3(s)}$

multi-component gas CH_4, CO_2, H_2

1.0 L of pore water

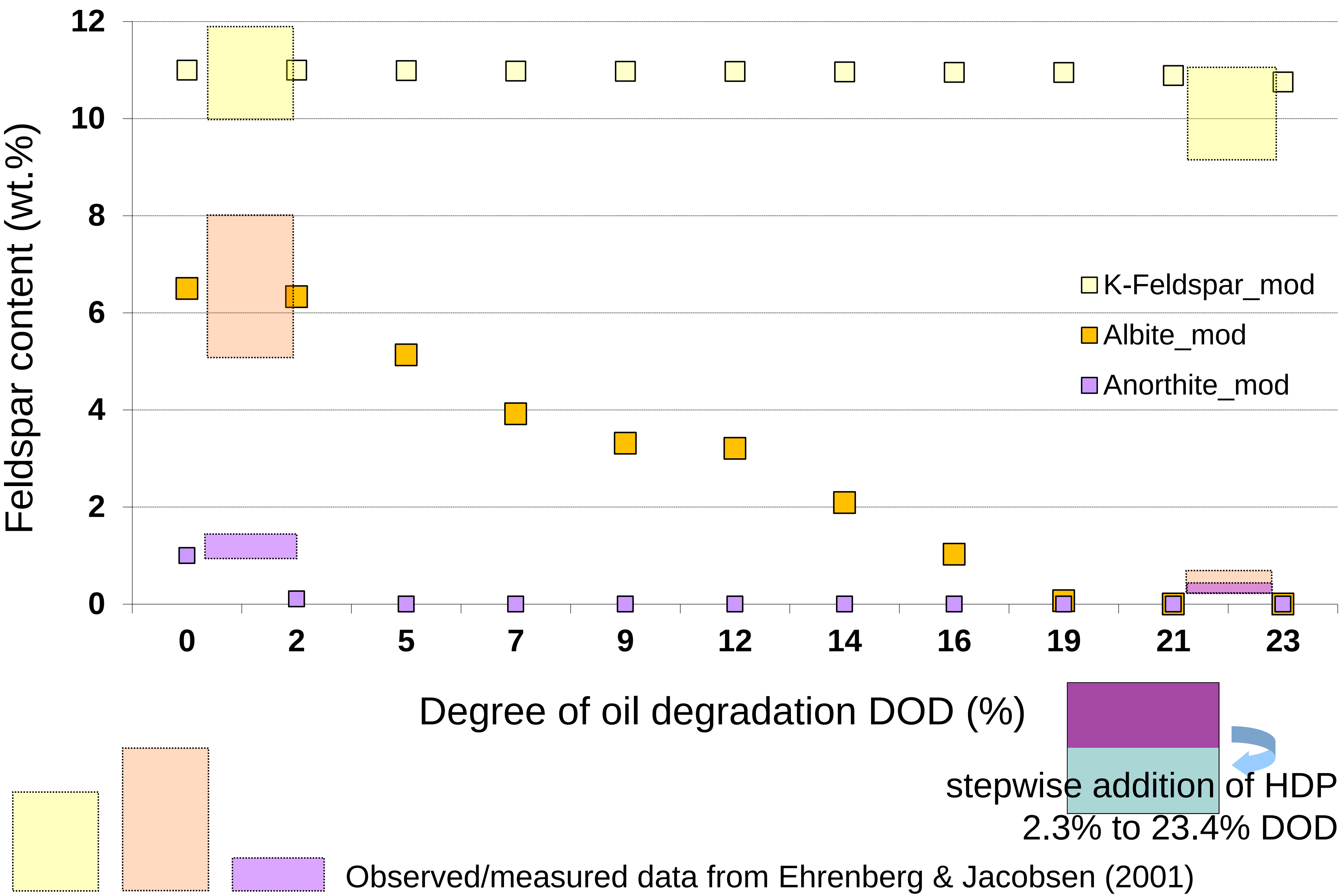
v_{tot} = 5 L **Water Reactor** **p_V = 1 L**

stepwise addition of HDP
2.3% to 23.4% DOD

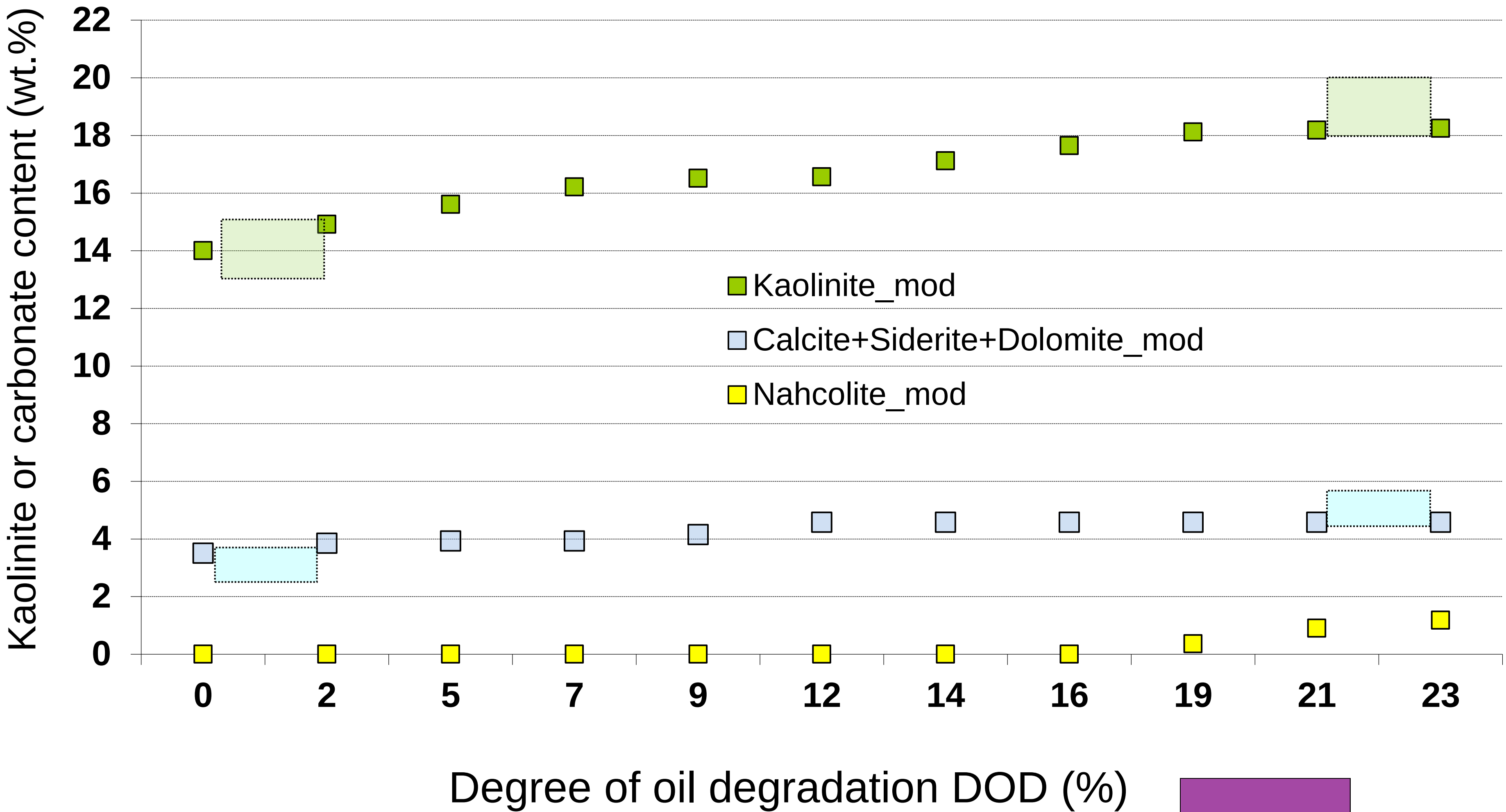
- equilibrium species distribution
- mass transfer

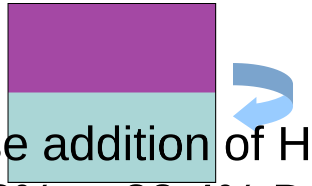
PHREEQC for Windows.lnk
US Geological Survey
Parkhurst and Appelo, 2009/2013

PHREEQC modeling results / alteration of the mineral assemblage (7)

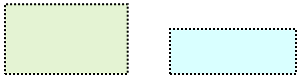


PHREEQC modeling results / alteration of the mineral assemblage (8)





stepwise addition of HDP
2.3% to 23.4% DOD

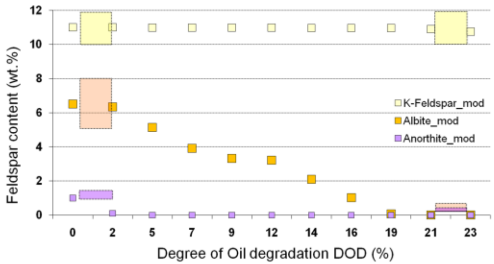


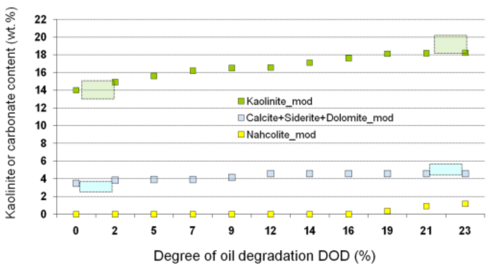
Observed/measured data from Ehrenberg & Jacobsen (2001)

PHREEQC modeling results (9)

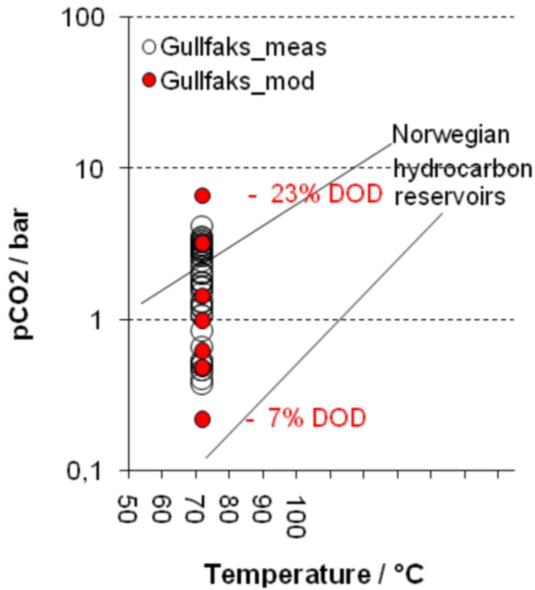
reproduce complex geochemical signals integrating the effects of oil degradation

measured data from Ehrenberg & Jakobsen (2001) and Smith & Ehrenberg (1989)





calculated pCO_2 in the multi-component gas

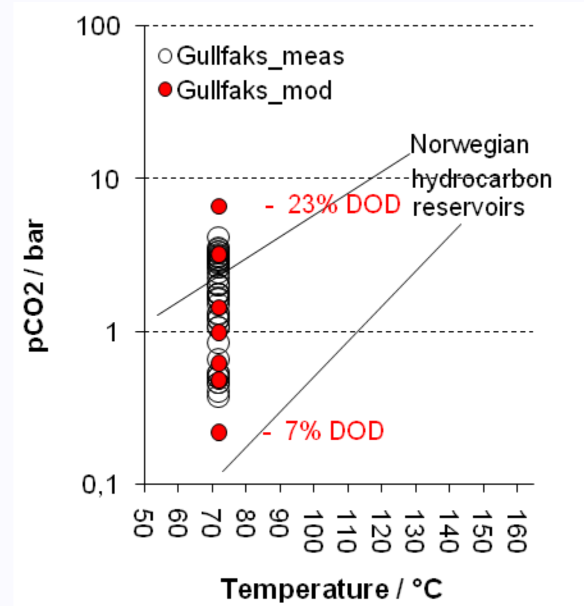


degree of oil degradation > 10% (Horstad et al., 1992)

Presenter's notes: Moreover, high degrees of oil degradation of about 20 % result in unusually high carbon dioxide pressures which have been observed by Smith & Ehrenberg.

Hydrogeochemical key factors affecting CO_2 content or partial pressure in gas

- amount of HDP (degree of oil degradation)
- type of equilibrating feldspar (sufficient amount)
- anorthite >> albite > K-feldspar
- amount of different feldspars in mineral assemblage
- amount of reducible Fe(III)-phases (goethite)
- formation of CO_2-sequestering sodium bicarbonate
- porosity (water or oil-to-rock ratio)
- type of HDP (acetic acid release) and of (initial) pore water



hydrogeochemical batch modeling helps to identify and quantify

* alteration of reservoir rock mineral phase assemblages (precip. / dissol.)

* thereby induced changes in porosity (& permeability)

* composition of multi-component gas

* composition of co-existing pore water

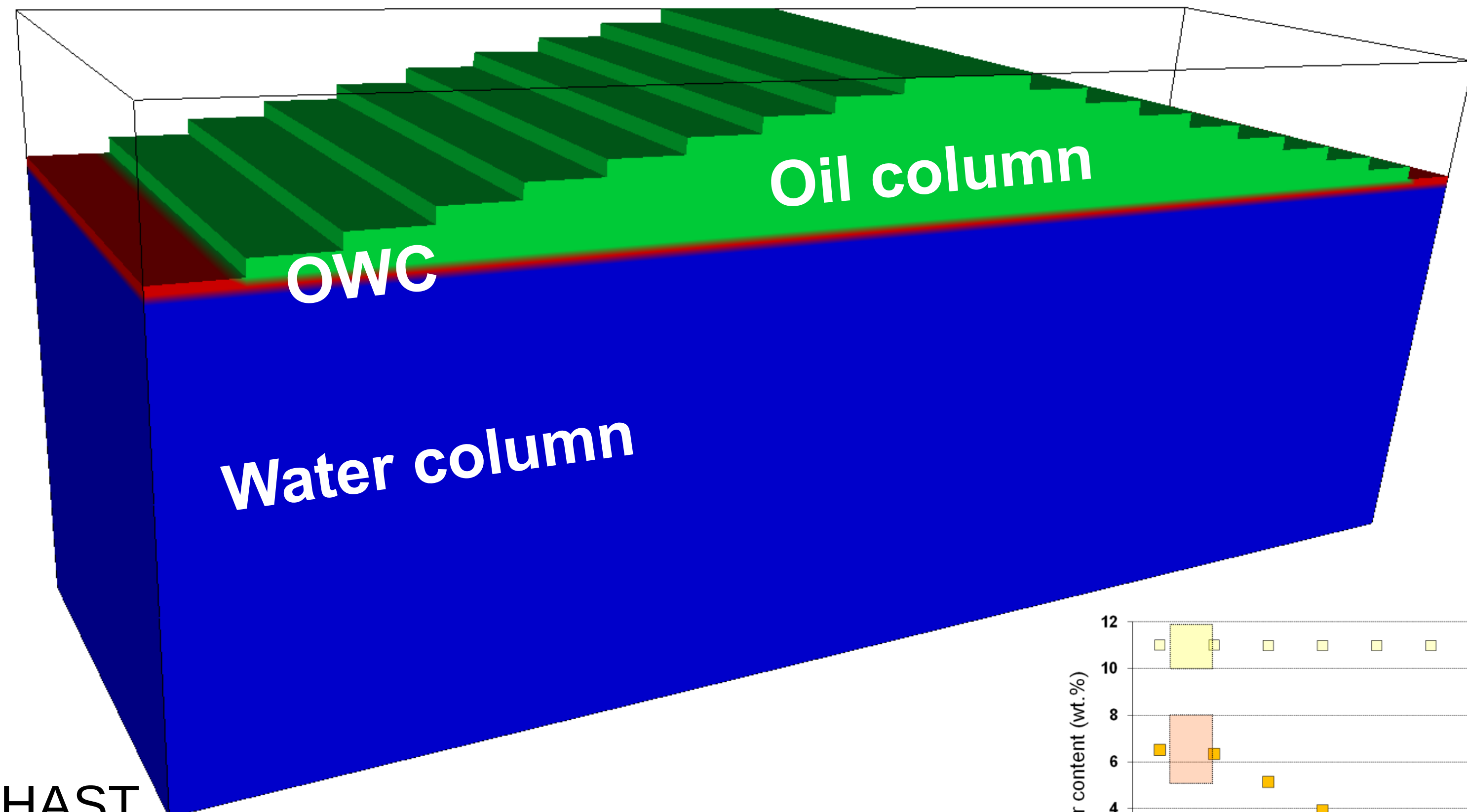
PHREEQC for Windows.lnk

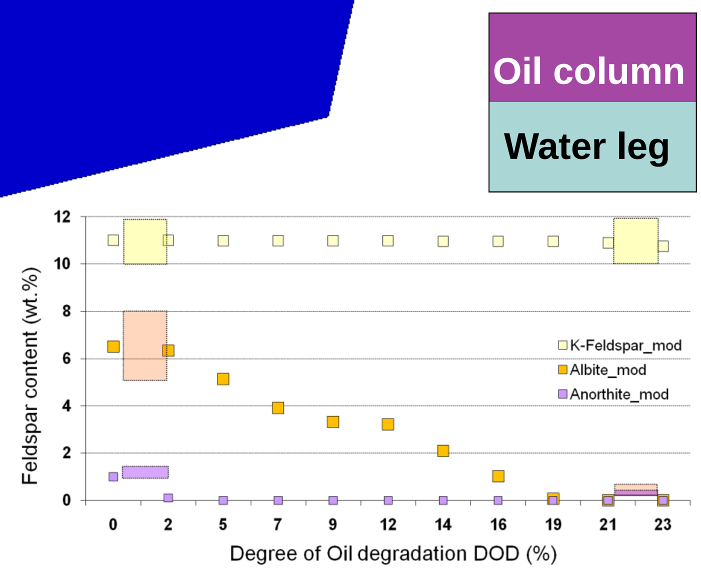
Gwb.ico

Organic-inorganic interactions controlling CO_2 fate and behavior

conceptual model / modeling tool / 3D reactive transport model (11)

to evaluate temporal and spatial developments in reservoir systems





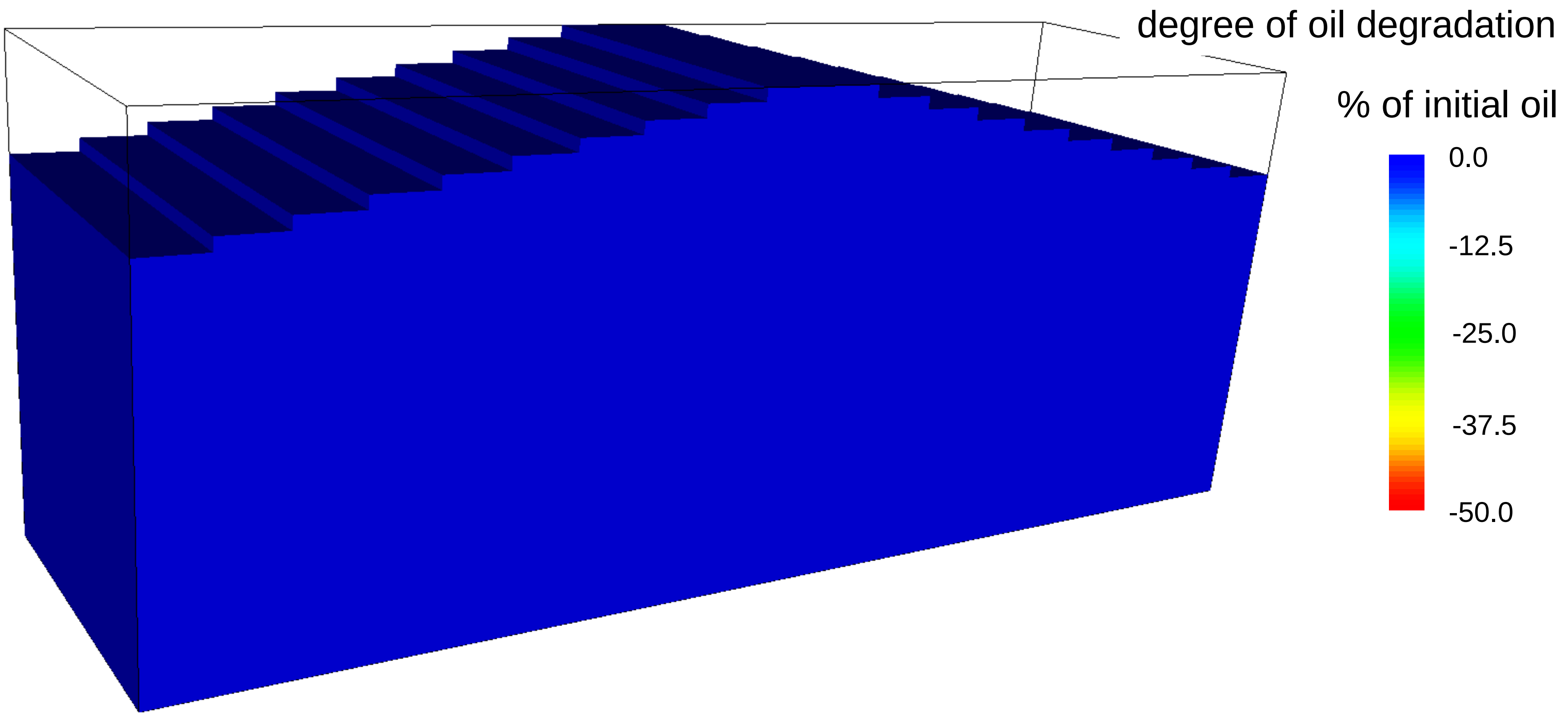
PHAST

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

USGS science for a changing world

PHREEQC.phrq

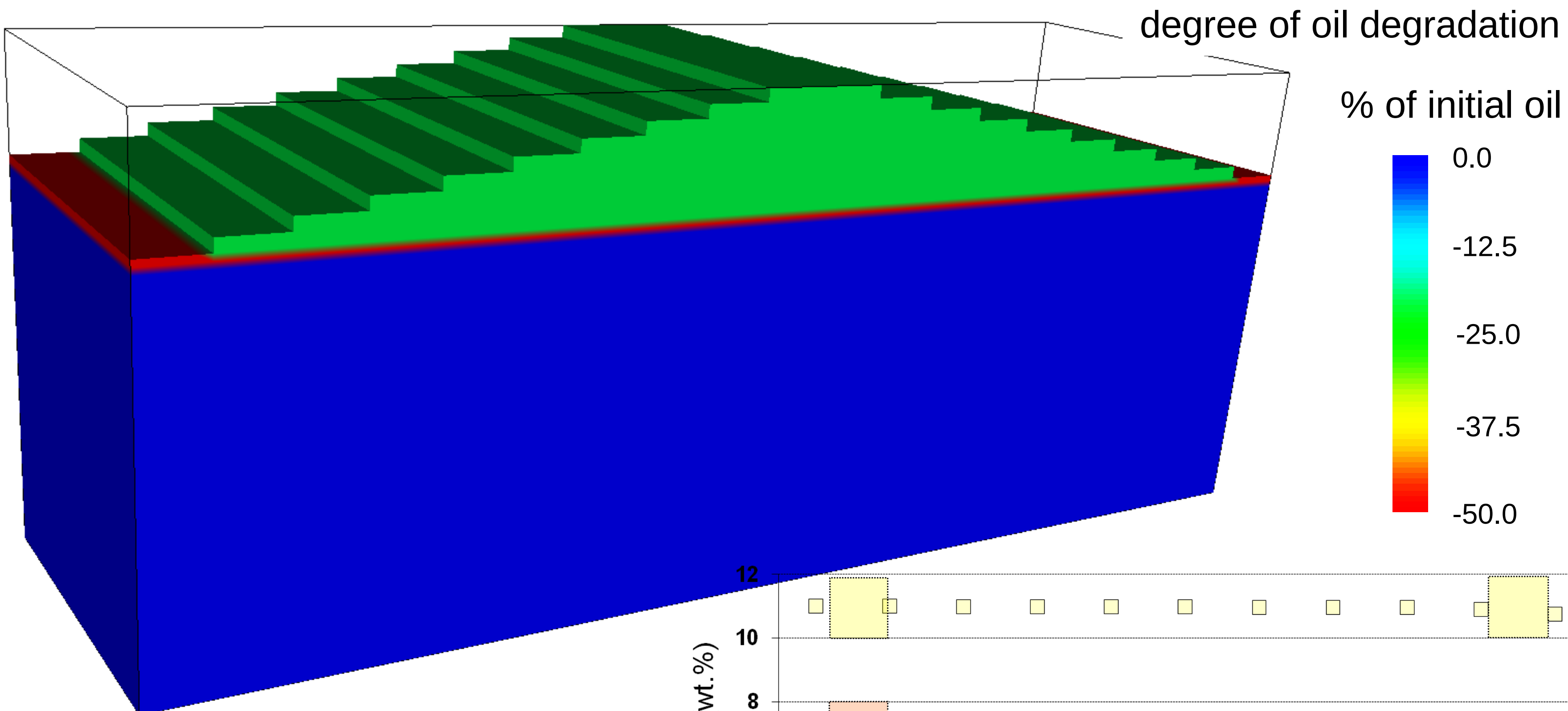
Horstad et al., 1992: degree of oil degradation > 10% (conservative estimate)



$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 4H_2O \rightarrow$
$R + 1.9CO_2 + 0.1CH_3COOH + 0.9CH_4 + 5H_2$
(Seewald, 2003)

modeling results / temporal and spatial development / degree of oil degradation (12)

Horstad et al., 1992: degree of oil degradation > 10% (conservative estimate)



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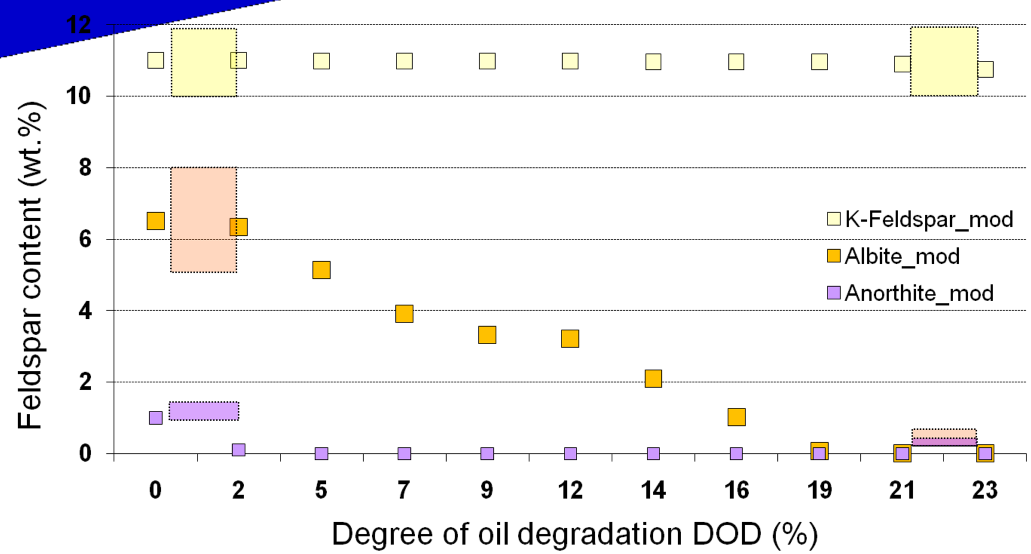
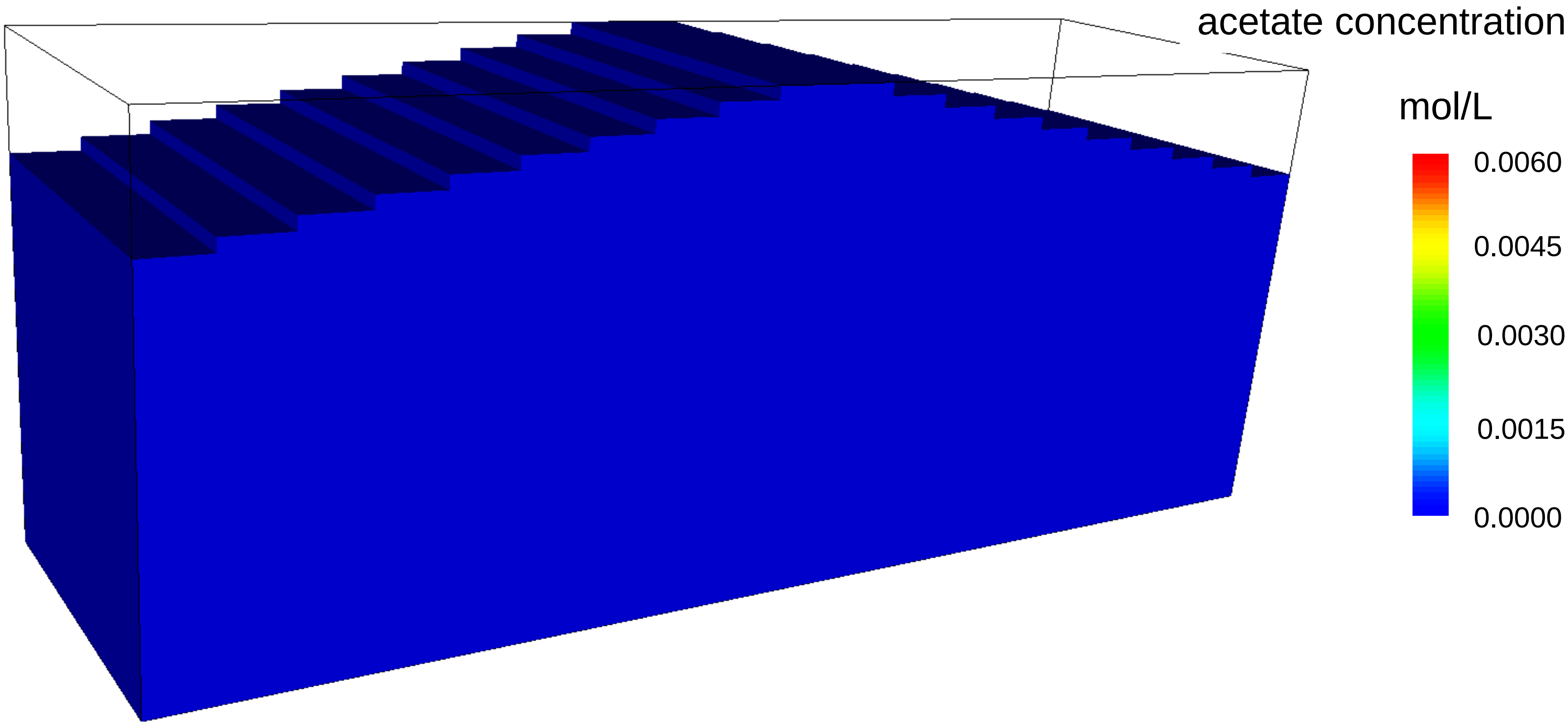
(Seewald, 2003)



aqueous concentration of acetate (13)



$$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 4H_2O \rightarrow R + 1.9CO_2 + 0.1CH_3COOH + 0.9CH_4 + 5H_2$$

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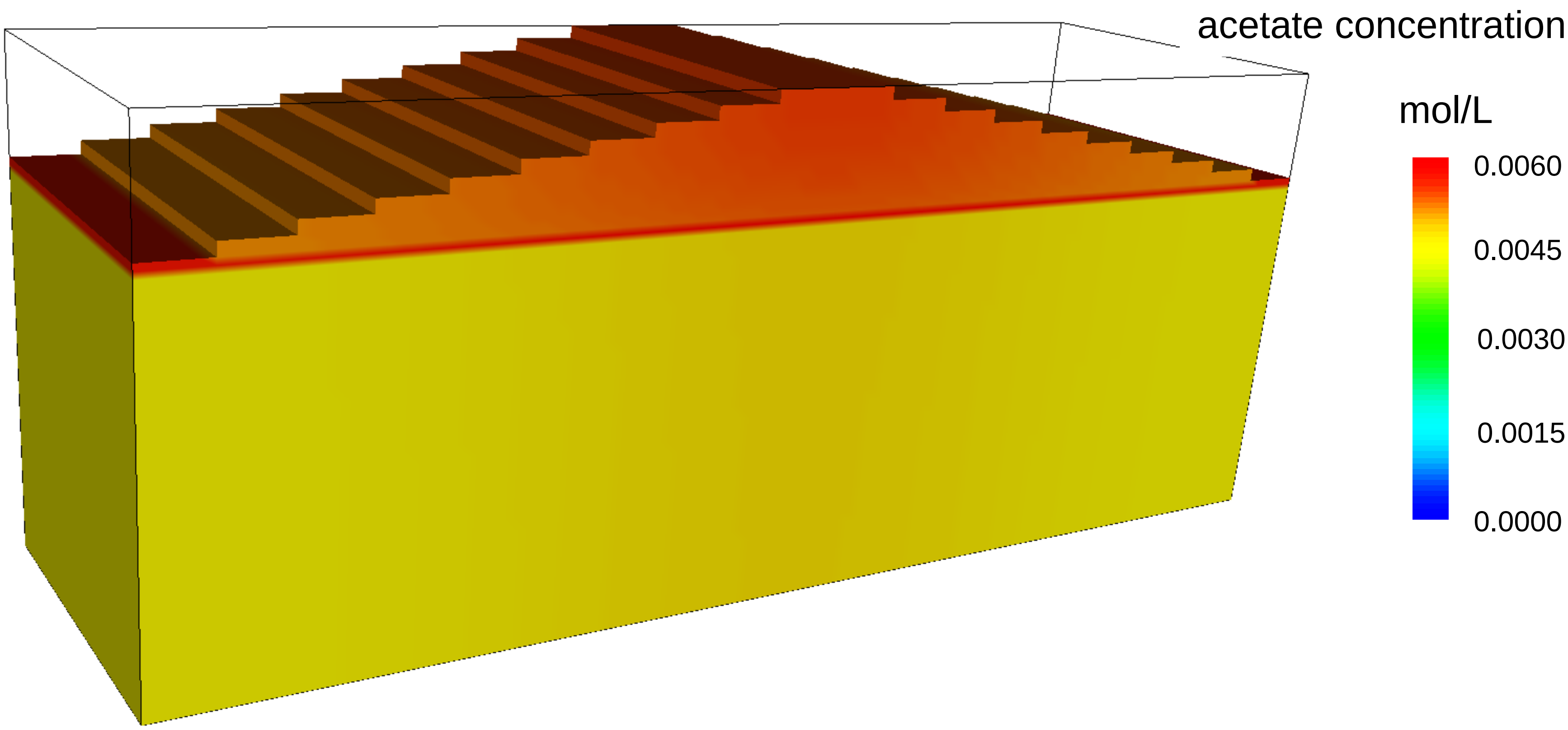

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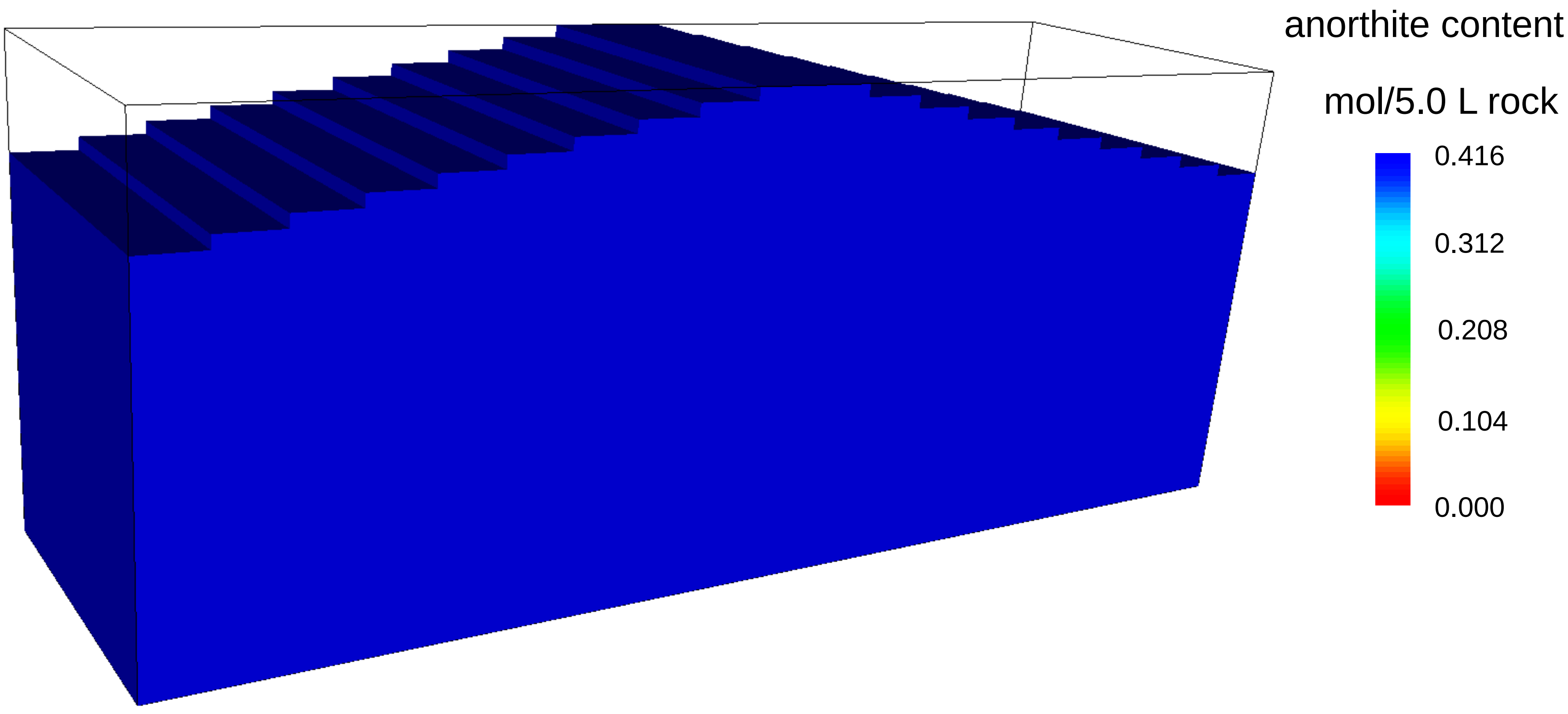
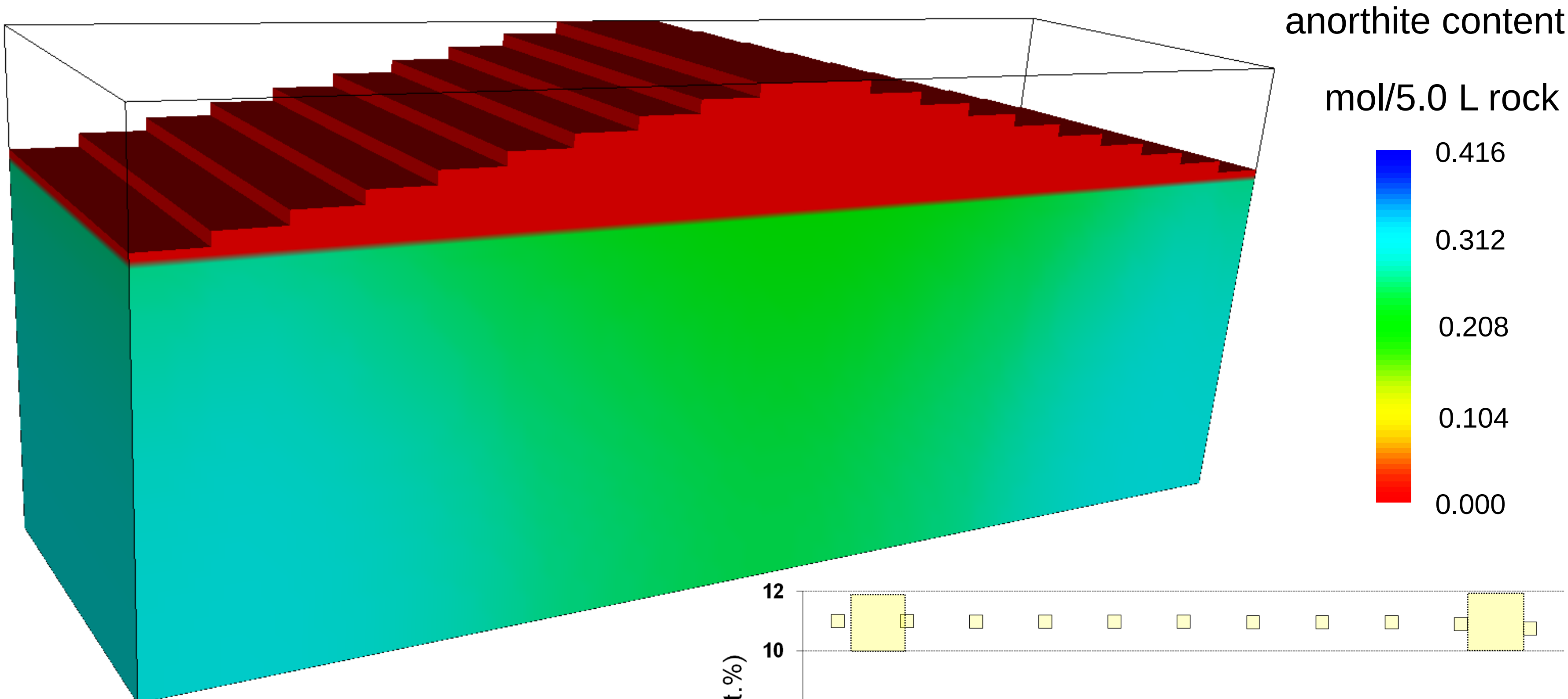
(Seewald, 2003)

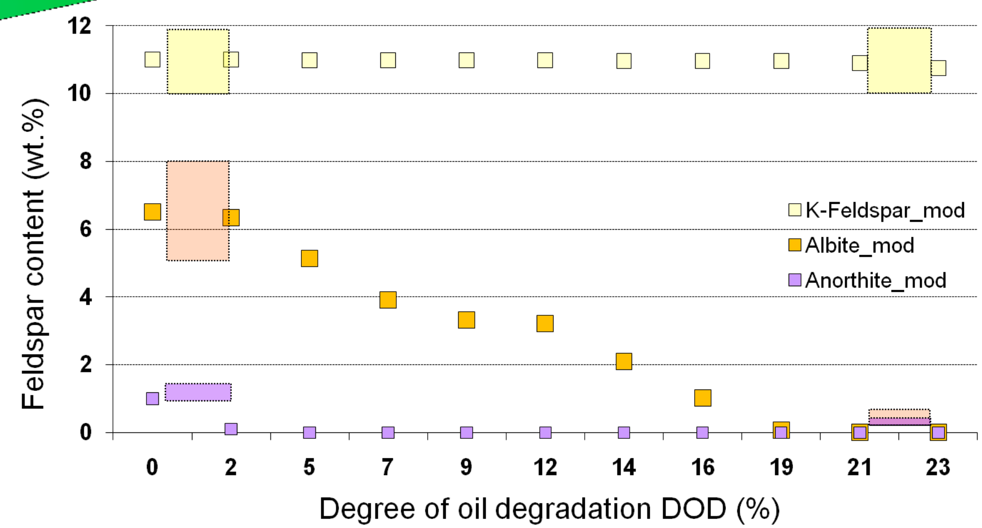
content of anorthite in reservoir rock (14)



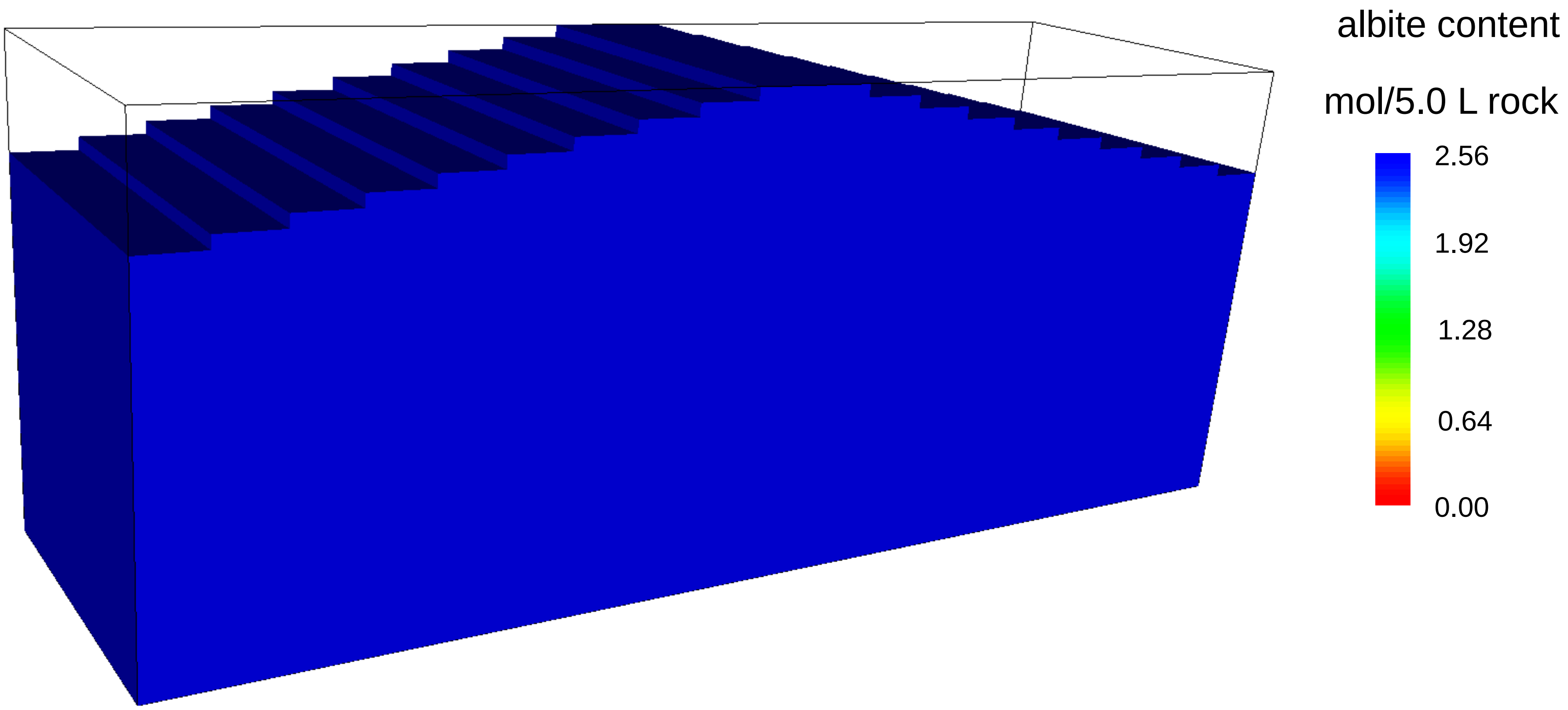
modeling results / temporal and spatial development

content of anorthite in reservoir rock (14)



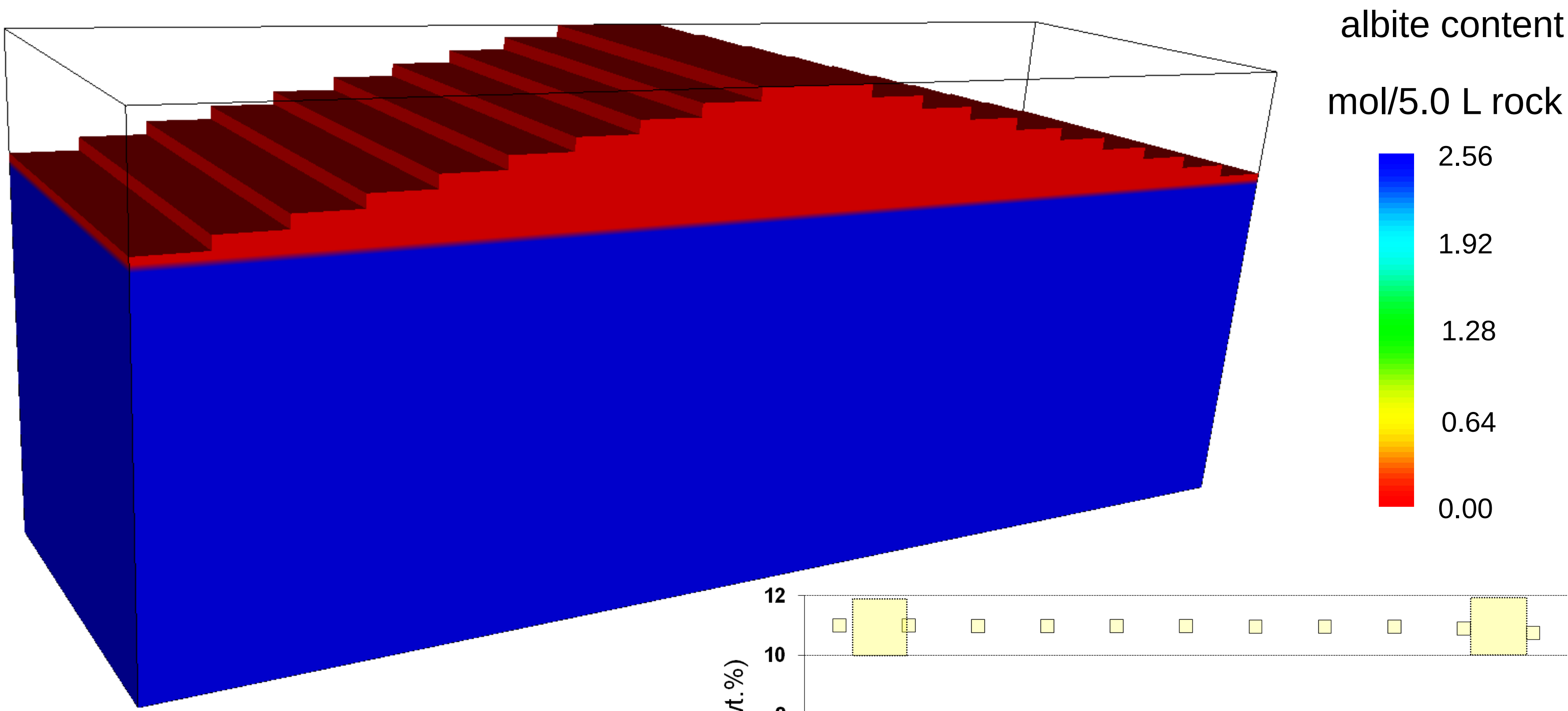


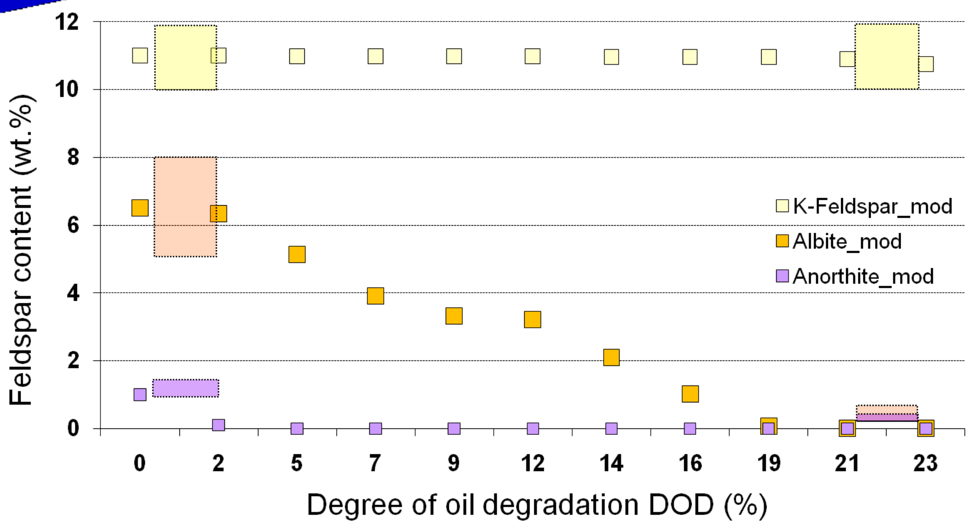
content of albite in reservoir rock (14)



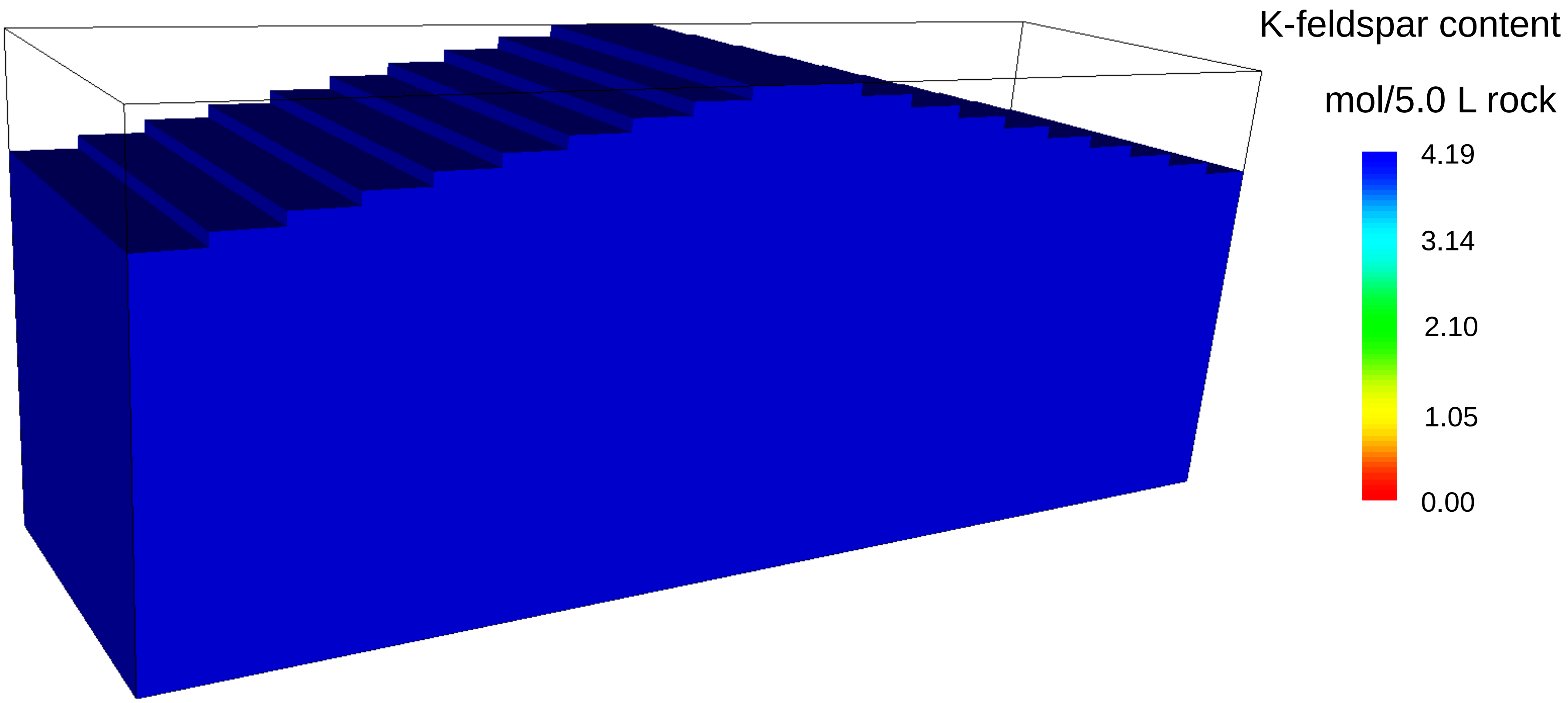
modeling results / temporal and spatial development

content of albite in reservoir rock (14)



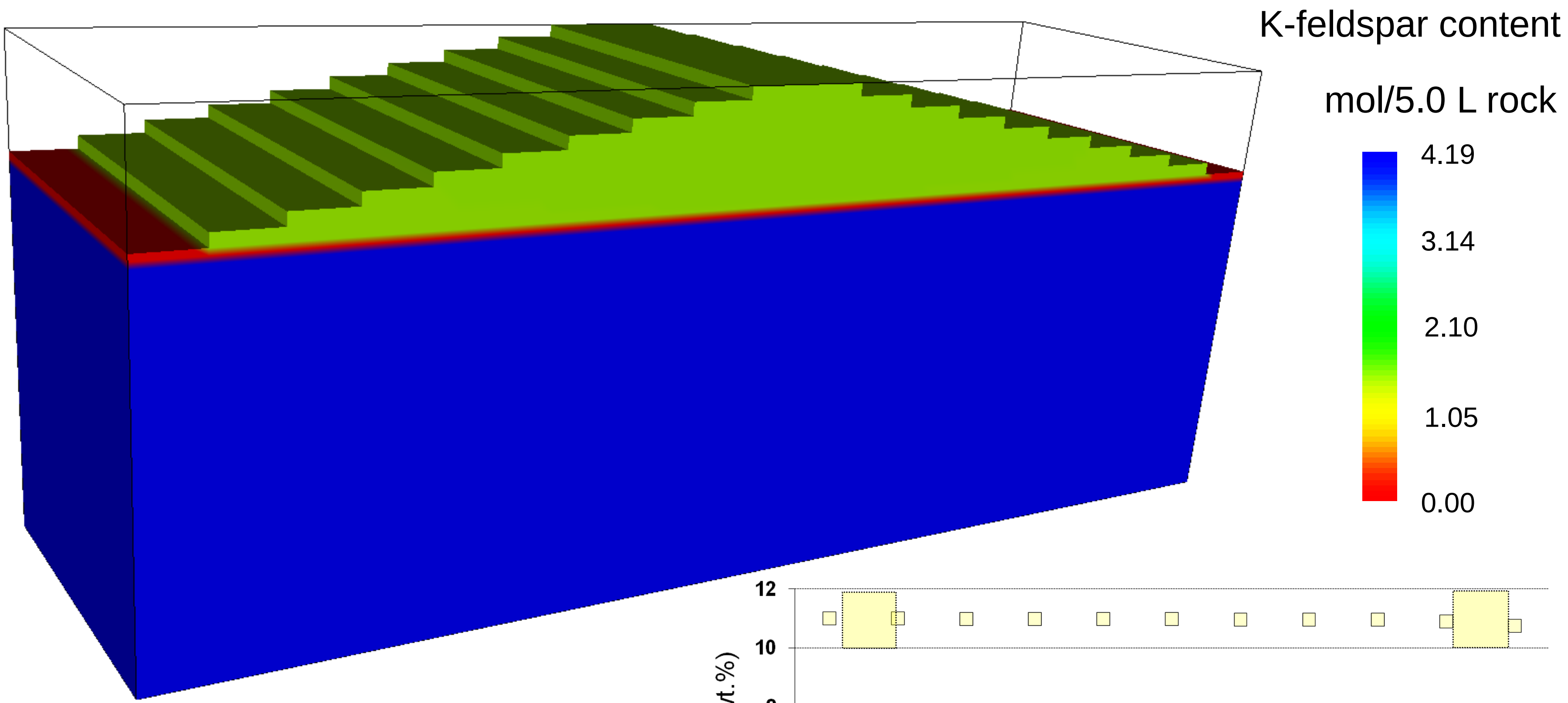


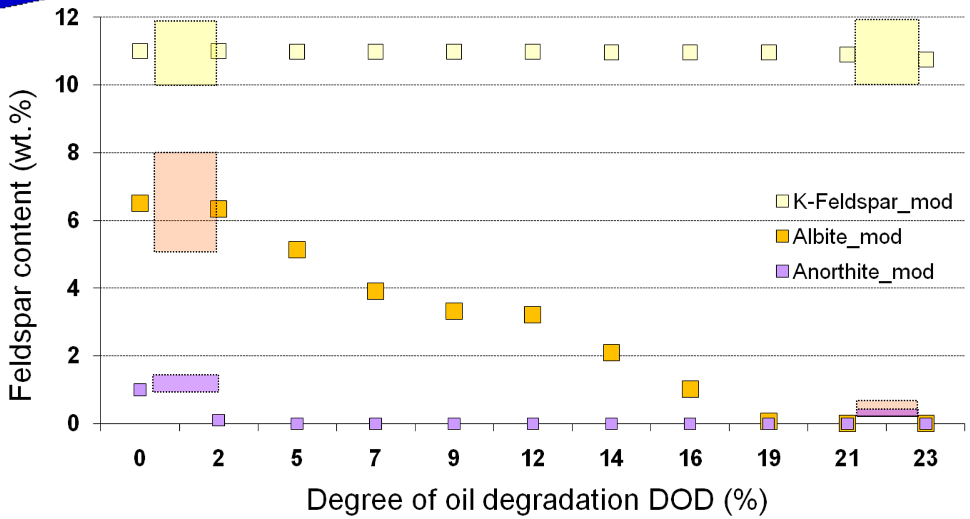
content of K-feldspar in reservoir rock (14)



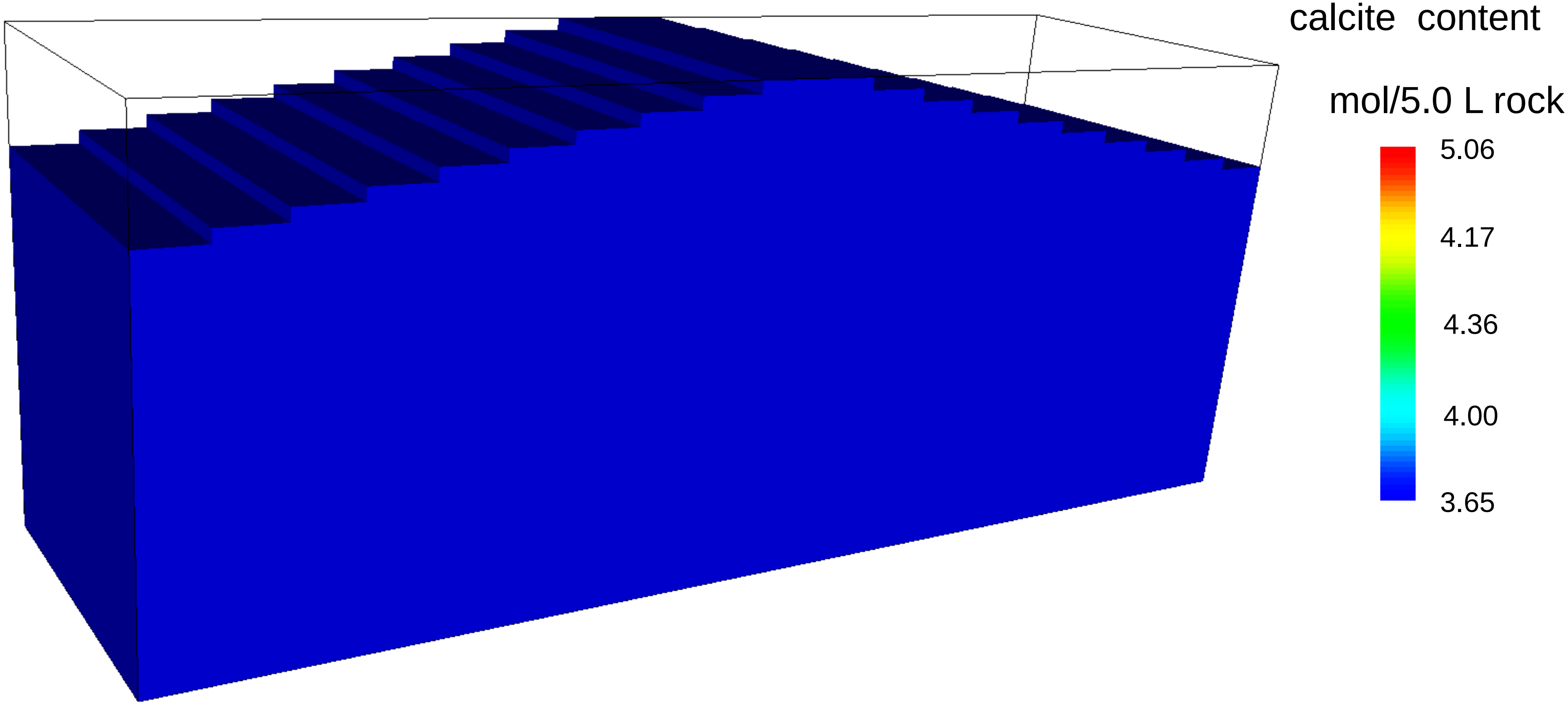
modeling results / temporal and spatial development

content of K-feldspar in reservoir rock (14)

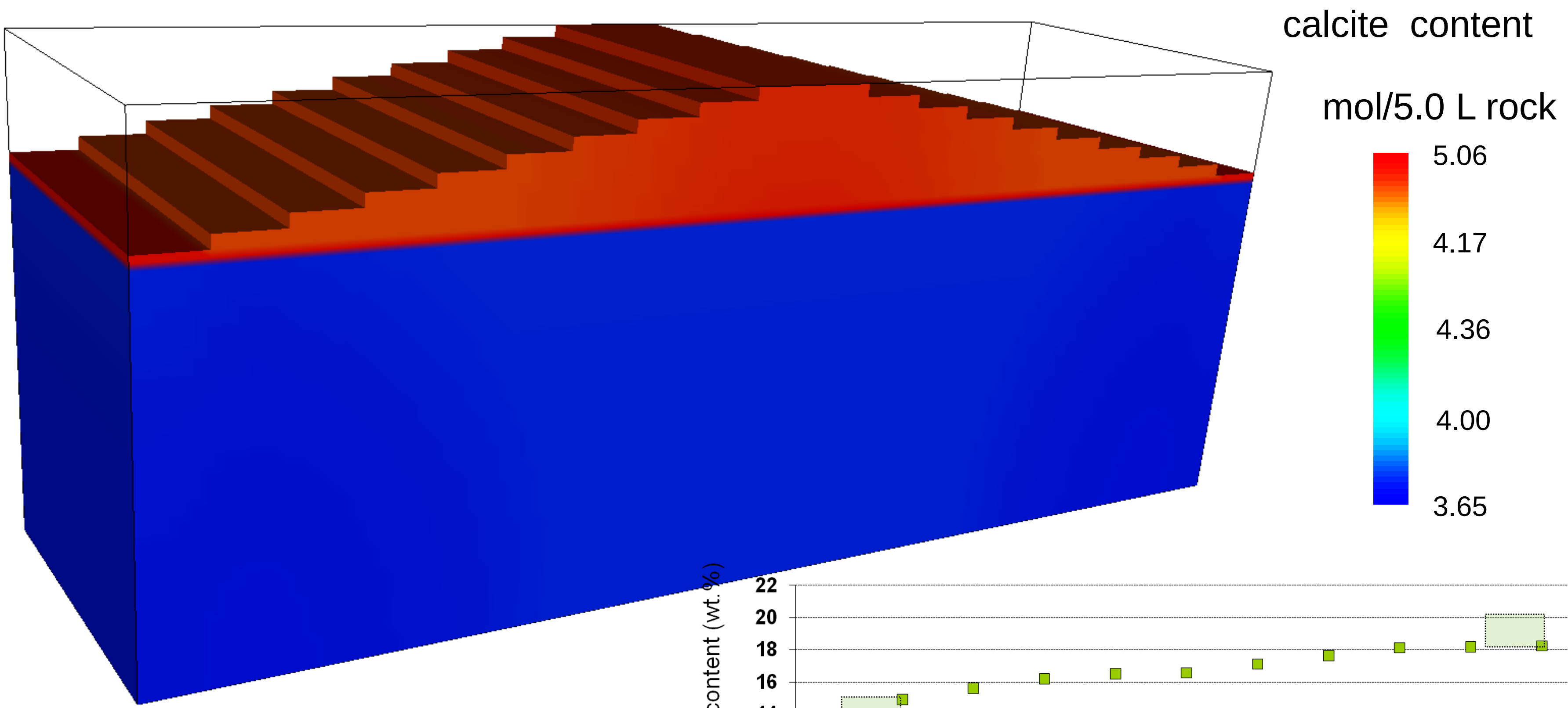


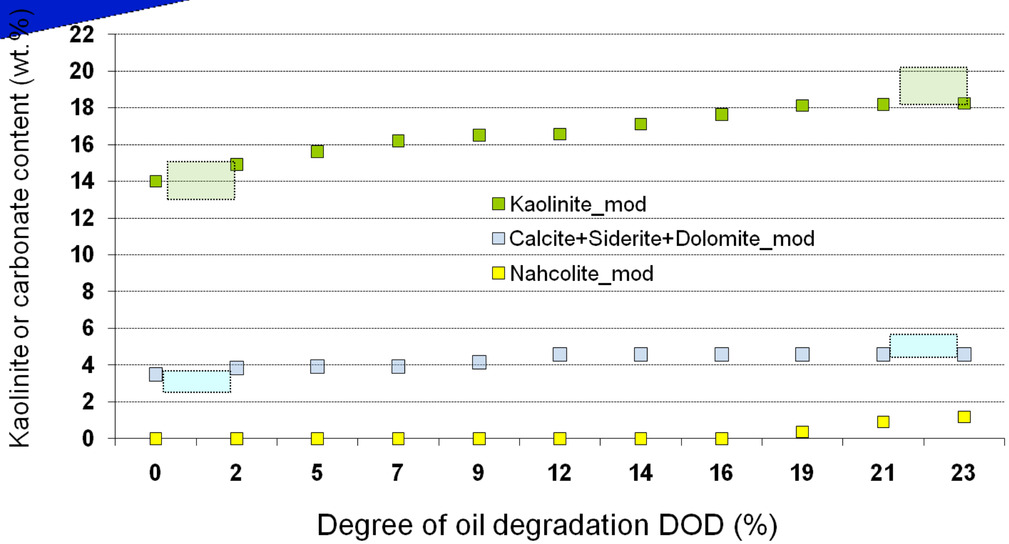


PHAST modeling results / content of calcite in reservoir rock (24)

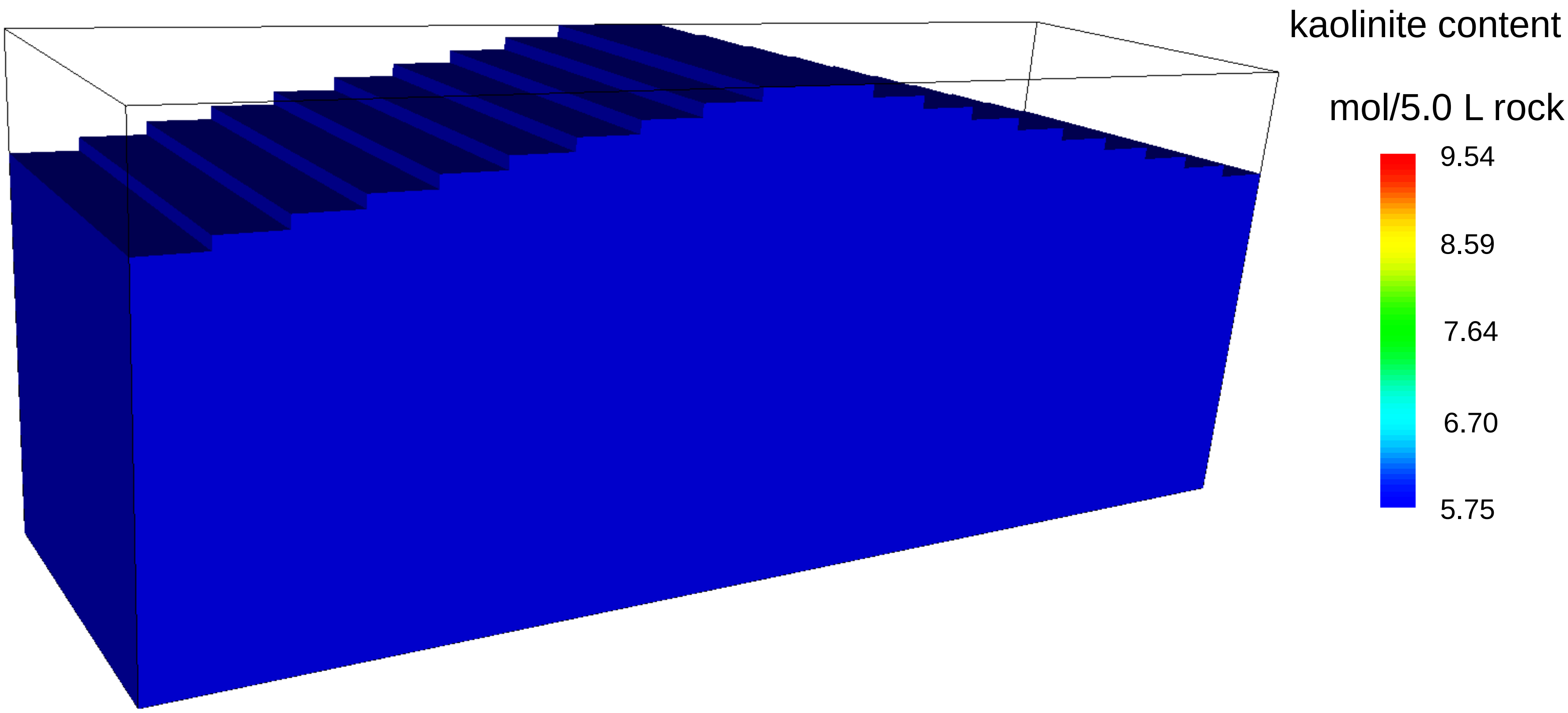


PHAST modeling results / content of calcite in reservoir rock (24)



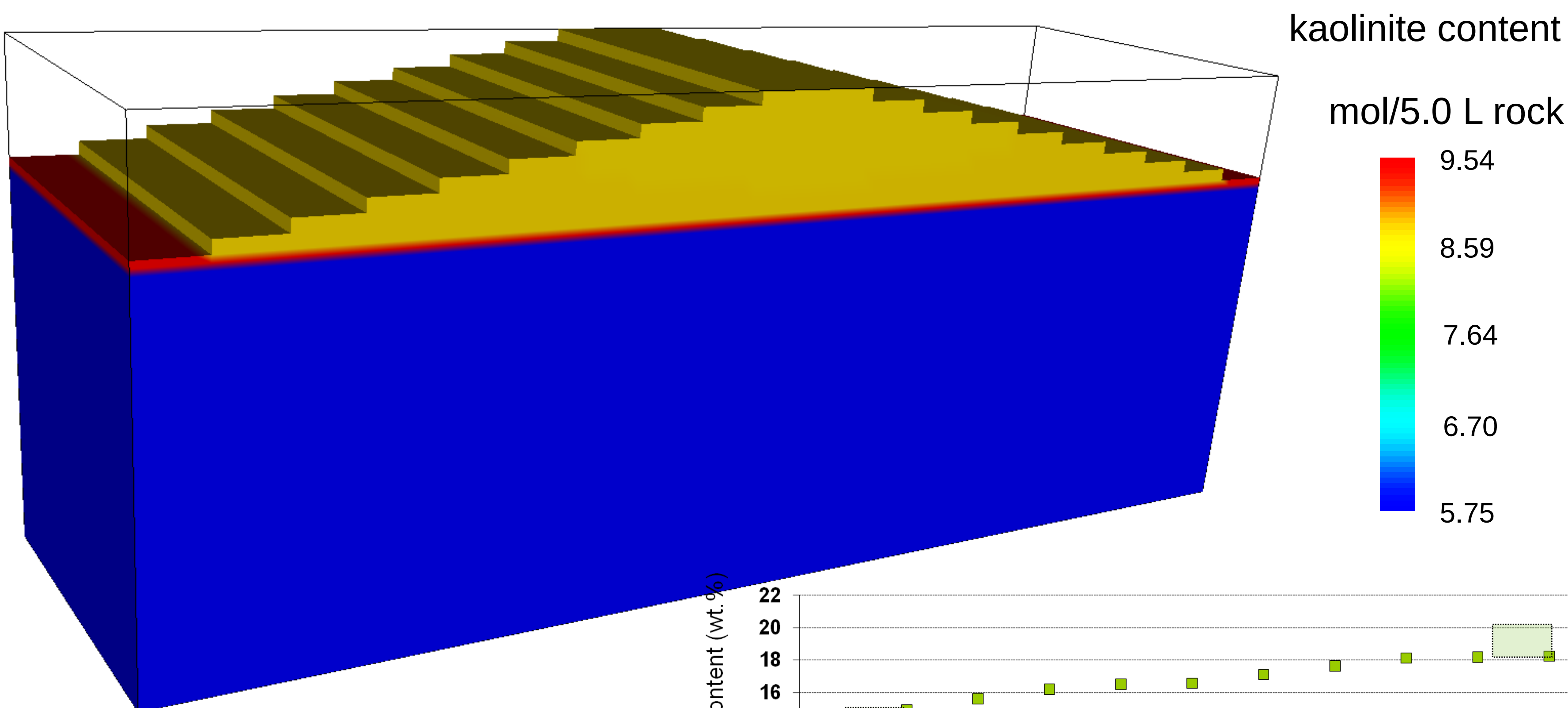


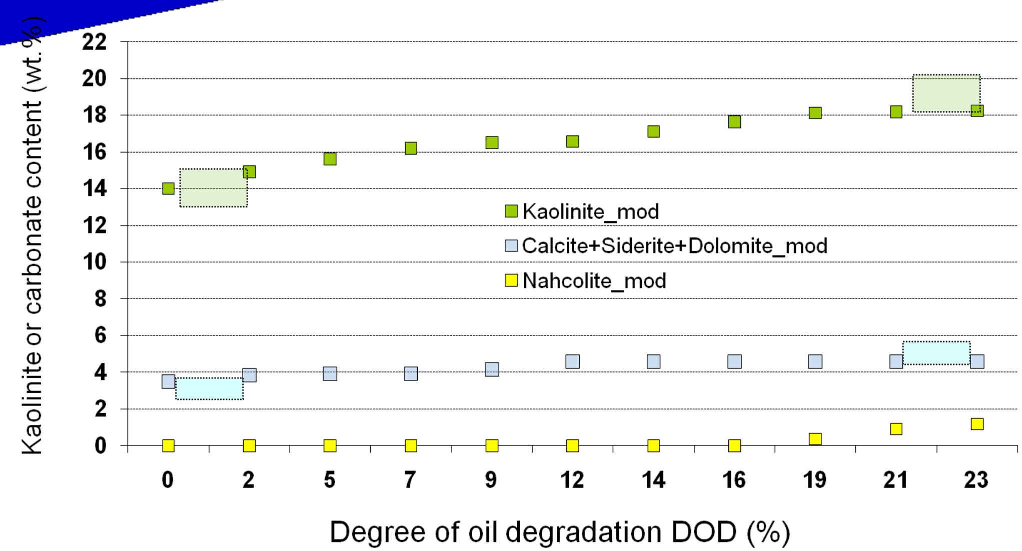
content of kaolinite in reservoir rock (14)



modeling results / temporal and spatial development

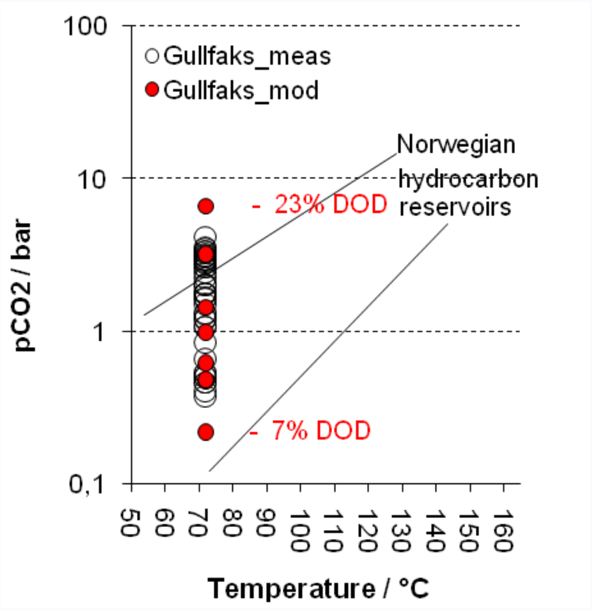
content of kaolinite in reservoir rock (14)





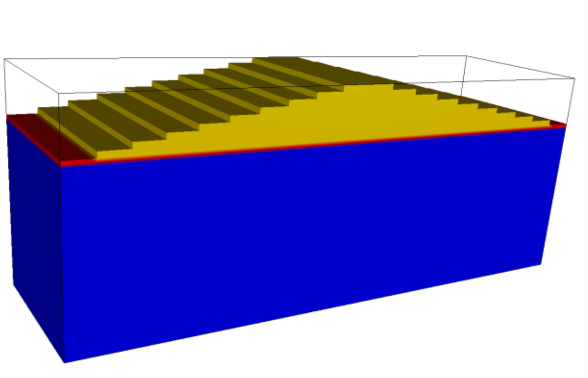
Conclusions / “0D” (batch) & **3D transport modeling** (18)

Hydrogeochemical key factors
affecting CO_2 content or partial pressure in gas



- amount of HDP (degree of oil degradation)
- type of equilibrating feldspar (sufficient amount)
- anorthite >> albite > K-feldspar
- amount of different feldspars in mineral assemblage
- amount of reducible Fe(III)-phases (goethite)
- formation of CO_2-sequestering sodium bicarbonate
- porosity (water or oil-to-rock ratio)
- type of HDP (acetic acid release) and of (initial) pore water

Hydrogeochemical modeling helps to identify and quantify



* alteration of mineral phase assemblages (precip. / dissol.)
* thereby induced changes in porosity (& permeability)
* **temporal & spatial developments**
* composition of multi-component gas phase
* composition of co-existing pore water