Intra-Reservoir Generation of Organic Acids and Late Stage Enhanced Porosity in Sandstones*

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Abstract

The source of organic acids is commonly attributed to the early maturation of kerogen in source rocks. Organic acids are frequently interpreted as the cause of burial-related secondary porosity. Major deficiencies of this concept are insufficient oxygen in the associated kerogen and likely deactivation of the acids already within the source rocks or during migration. Experimental studies by Eglinton et al. (1987) and Seewald (2001, 2003) proved the generation of significant amounts of water-soluble organic acids (carboxylic acids) by oxidation of n-alkanes. This implies that oxidation of oil compounds and generation of organic acids is likely to occur not only in source rocks but even more effectively along migration paths and in reservoirs. We aim at supplementary experimental work, based on a wealth of field observations and lab data from Permian red-bed reservoir sandstones in the Central European Basin. We want to evaluate the hypothesis that liquid hydrocarbons in hematitic reservoirs can generate reactive organic acids and/or CO_2 during post-emplacement thermal evolution. The expected outcome could allow a better understanding of late stage (syn- and post-oil) porosity enhancement in deep basinal settings with methane source/reservoir potential (tight gas plays).

Session: Sandstone Diagenesis and Reservoir Quality (SEPM)

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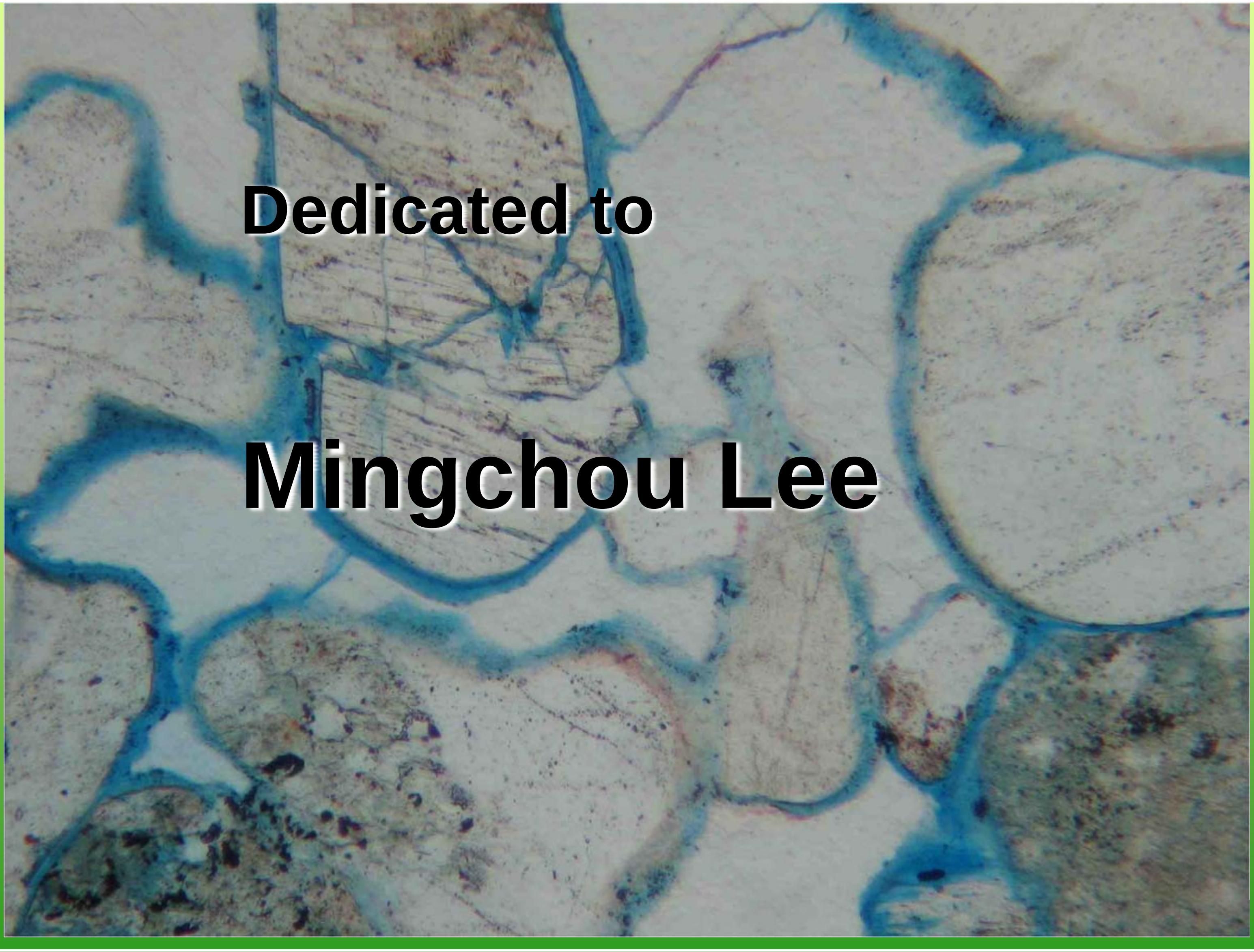
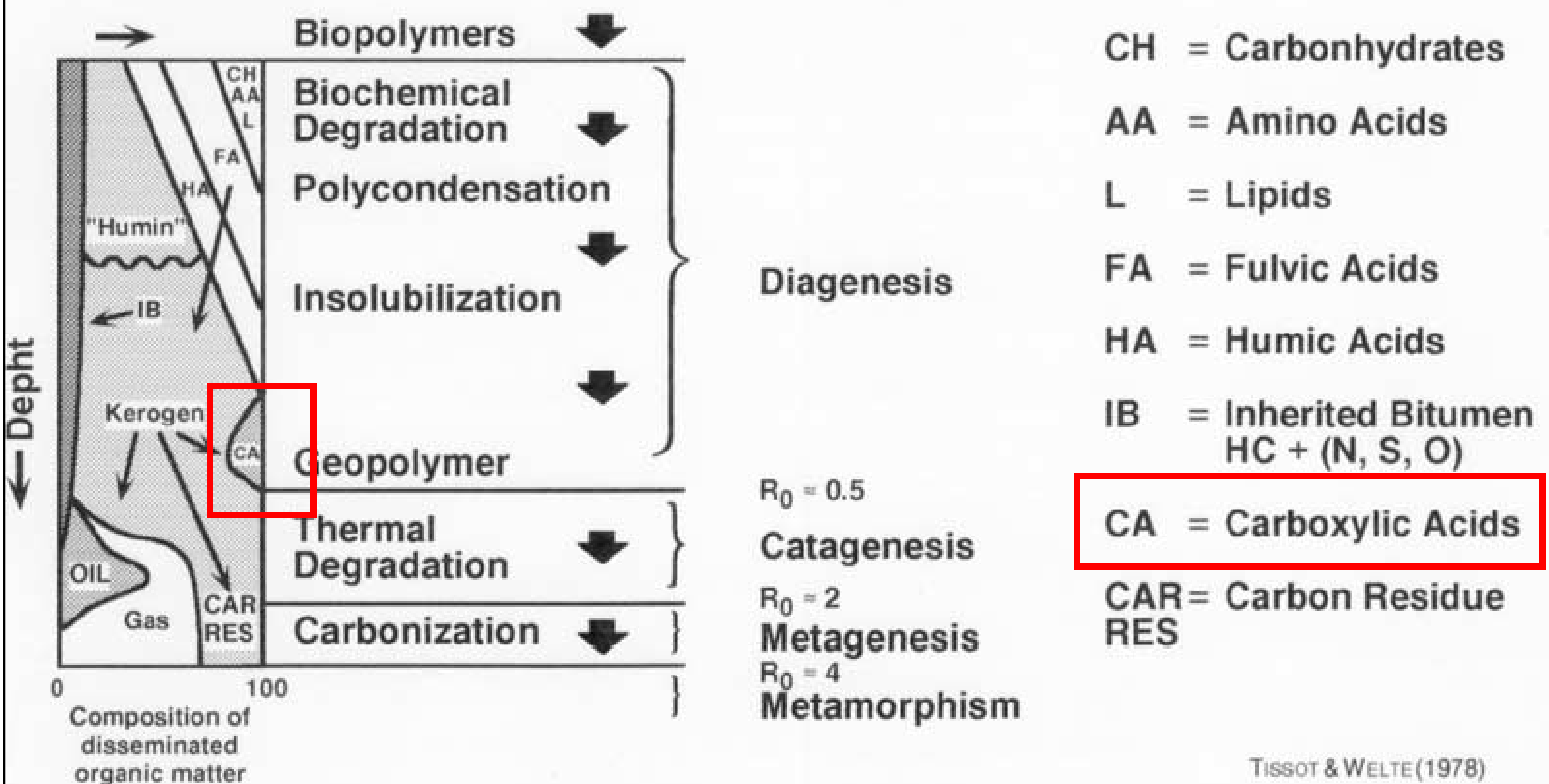
with contributions by A. Meier, R. Lippmann, E. Kiefer



Dedicated to

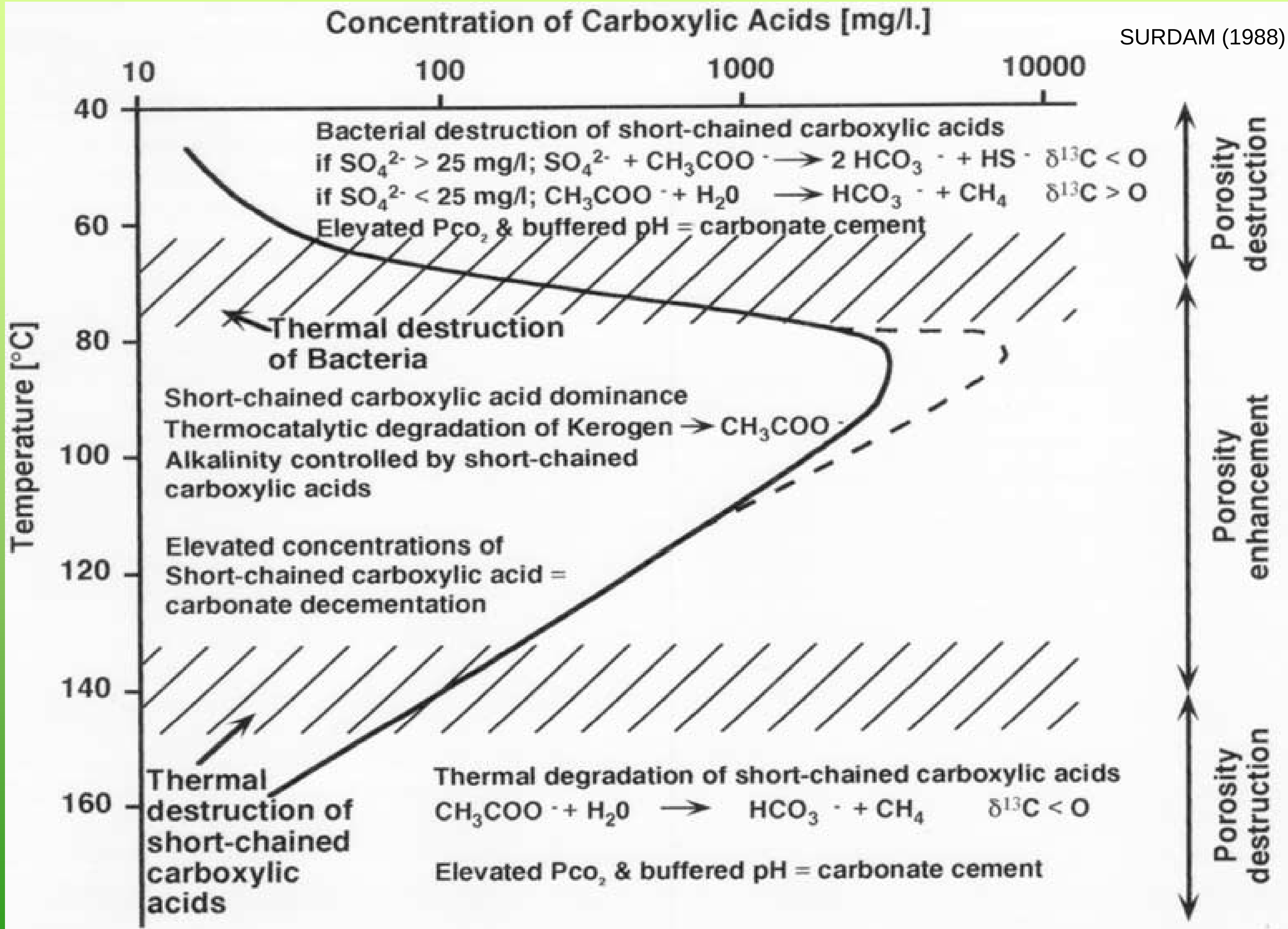
Mingchou Lee

An old topic?



Biopolymers
Biochemical Degradation
Polycondensation
Insolubilization
Geopolymer
Thermal Degradation
Carbonization
CH
AA
L
FA
HA
"Humin"
IB
Kerogen
CA
OIL
Gas
CAR
RES
Depht
0
100
Composition of disseminated organic matter
Diagenesis
R_0 = 0.5
Catagenesis
R_0 = 2
Metagenesis
R_0 = 4
Metamorphism
CH = Carbonhydrates
AA = Amino Acids
L = Lipids
FA = Fulvic Acids
HA = Humic Acids
IB = Inherited Bitumen HC + (N, S, O)
CA = Carboxylic Acids
CAR RES = Carbon Residue
Tissot & Welte (1978)

An old topic?



Concentration of Carboxylic Acids [mg/l.]
SURDAM (1988)
10
100
1000
10000
40
60
80
100
120
140
160
Temperature [°C]
Bacterial destruction of short-chained carboxylic acids
if SO_4^{2-} > 25 mg/l; SO_4^{2-} + CH_3COO^- → 2 HCO_3^- + HS^- $\delta^{13}C < O$
if SO_4^{2-} < 25 mg/l; CH_3COO^- + H_20 → HCO_3^- + CH_4 $\delta^{13}C > O$
Elevated Pco_2 & buffered pH = carbonate cement
Thermal destruction of Bacteria
Short-chained carboxylic acid dominance
Thermocatalytic degradation of Kerogen → CH_3COO^-
Alkalinity controlled by short-chained carboxylic acids
Elevated concentrations of Short-chained carboxylic acid = carbonate decementation
Thermal destruction of short-chained carboxylic acids
Thermal degradation of short-chained carboxylic acids
CH_3COO^- + H_20 → HCO_3^- + CH_4 $\delta^{13}C < O$
Elevated Pco_2 & buffered pH = carbonate cement
Porosity destruction
Porosity enhancement
Porosity destruction

Carboxylic acids were considered as cause of secondary porosity (e.g. Surdam et al.1988)

Less attention paid to carboxylic acids since late 80s

Major deficiency of concept:
Organic acids form within source rocks and become deactivated by metall-cations during migration

We predict generation of organic acids within reservoir as reaction product between oil (n-alkanes) and oxidants

Outline

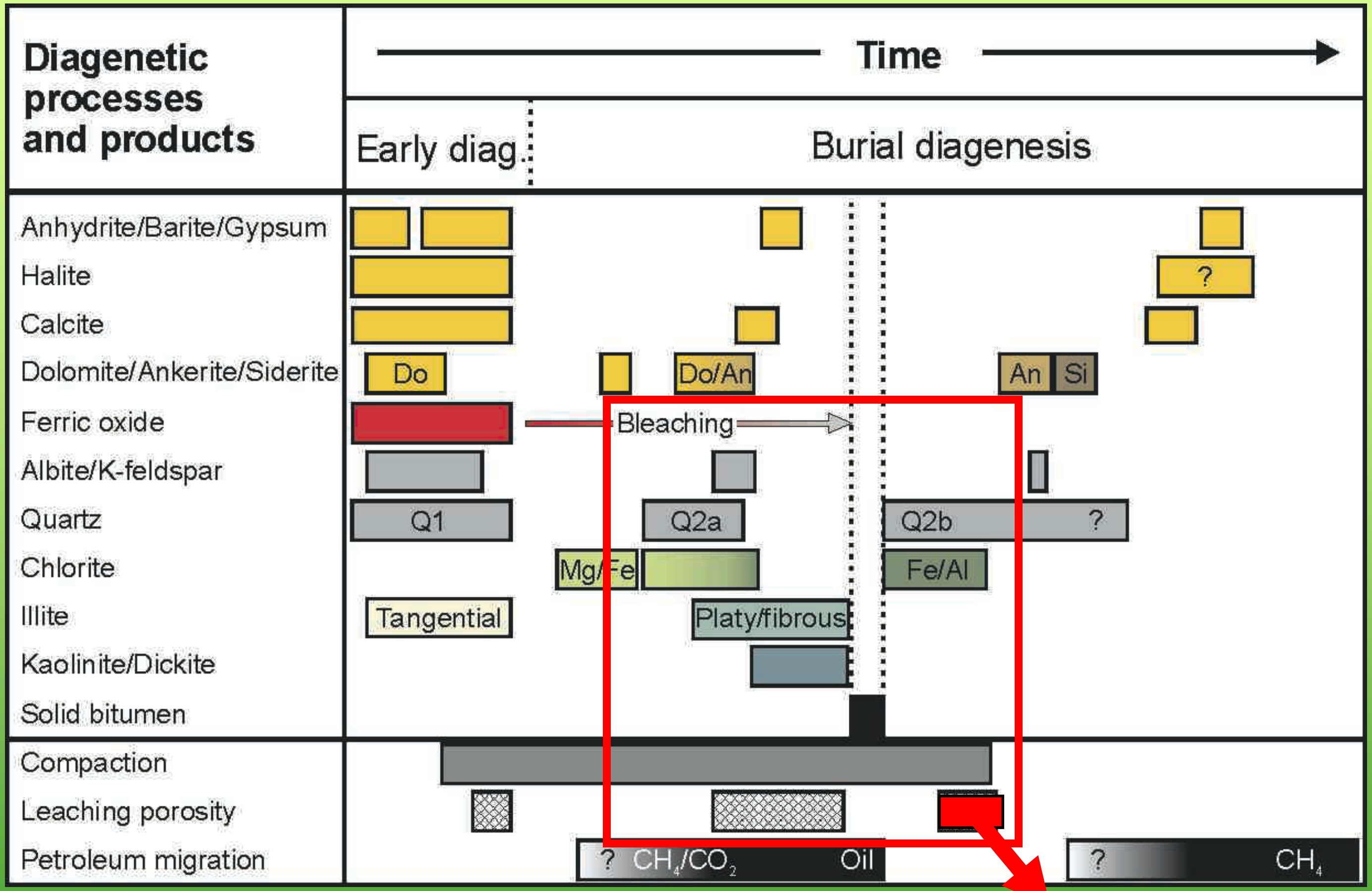
Cases where present gas reservoirs were former oil reservoirs or HC migration pathways

Examples from Permian and Triassic red beds
(North Sea Central Graben, NL on- and offshore, Germany, Poland)

Observations

1. **Partial or total bleaching of red beds, clay growth**
2. **Oil impregnations ⇒ bitumen staining**
3. **Feldspar and lithoclast dissolution after the hydrocarbon immigration**
4. **Thermal and maturation modelling indicates T >120°C, K/Ar dating of authigenic illite points to late burial stage**

Paragenetic sequences



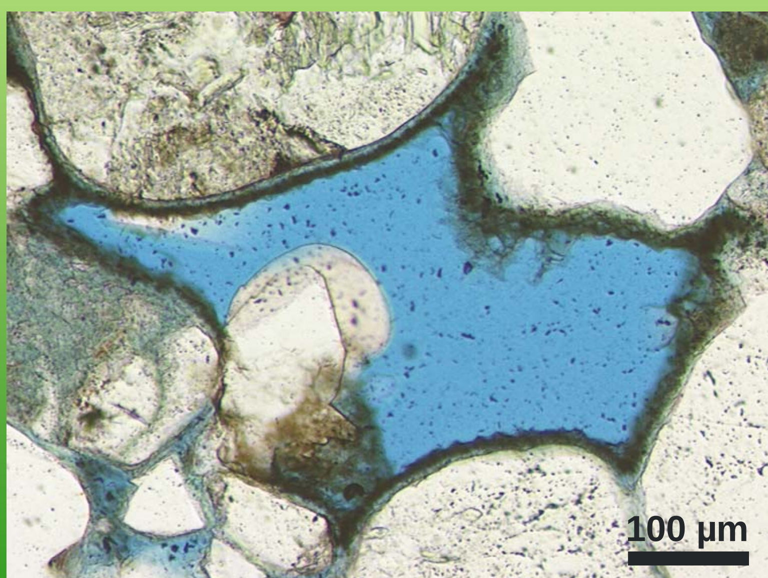
Late secondary porosity (enhanced porosity)

Mineral reactions related to “ maturing source rocks“

within the reservoir:

... microscopic scale

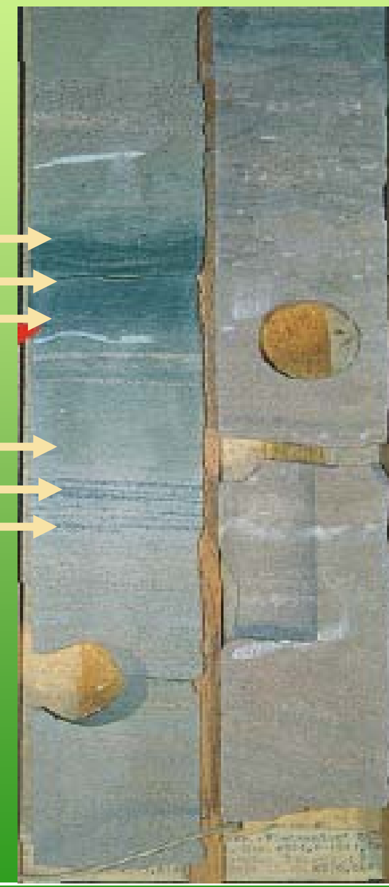
⇒ bleaching
⇒ kaolinite, illite, chlorite
⇒ bitumen
⇒ late secondary porosity



... core scale

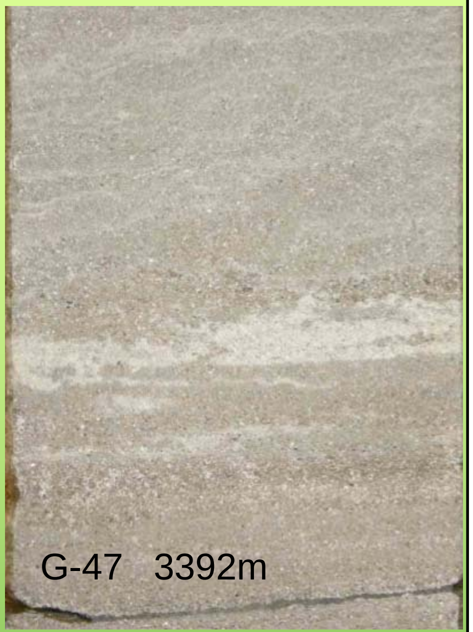
bitumen

bitumen



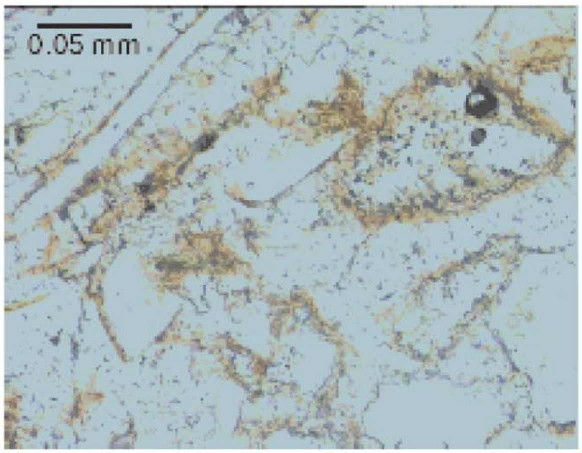
from Gaupp et al. (2005)

Bleaching in red beds:



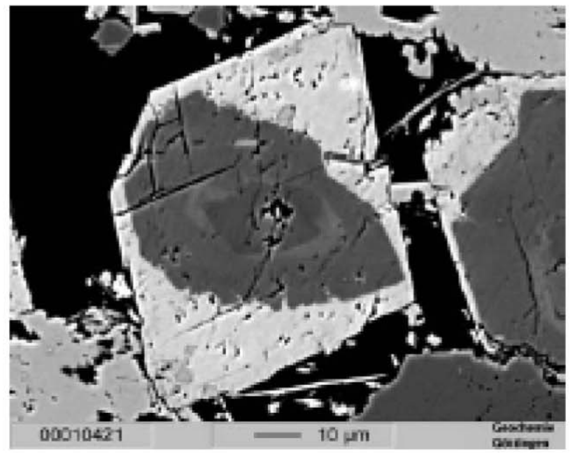
Bleaching and Fe transfer

Reduction of Fe-oxides

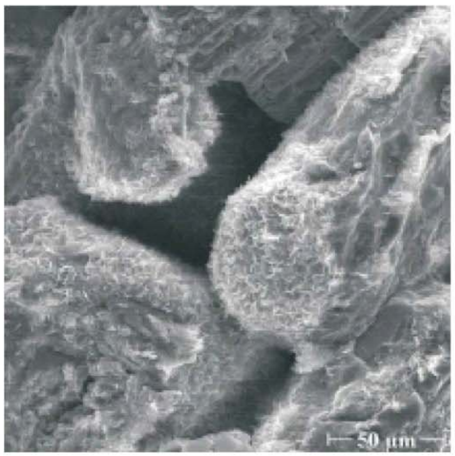


Hematite coatings preserved in a carbonate nodule

Fe(II) bearing mesodiagenetic phases



Fe-carbonate (white) postdates Nonferrous carbonate (gray)



Euhedral grain-rimming chlorite

Reduction/bleaching of iron (hematite coats)
→ authigenic clays → oil immigration
→ porosity enhancement

Lippmann (2006)

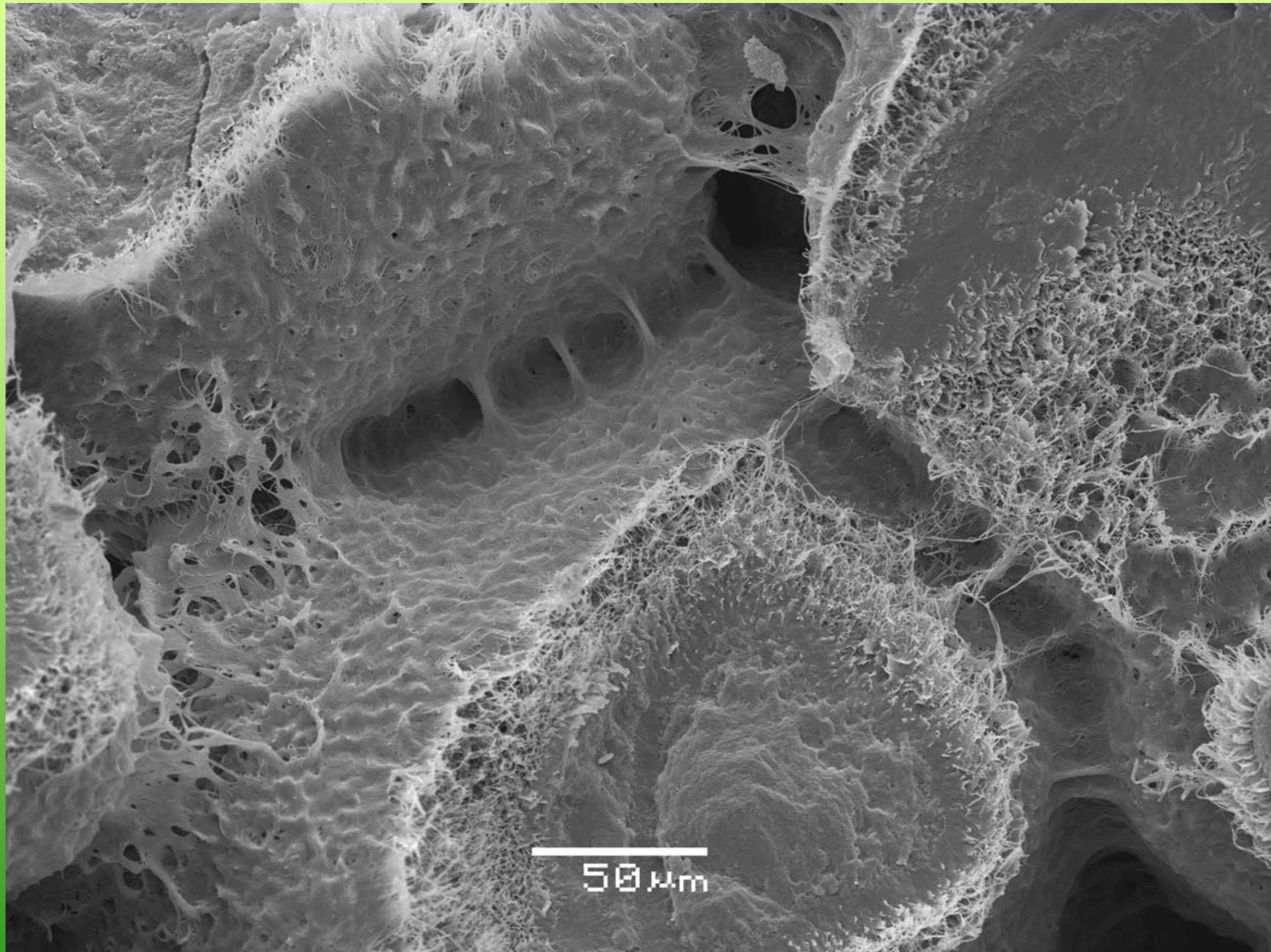
Consequences of Bleaching:

Cleaning of migration pathways and parts of the reservoirs

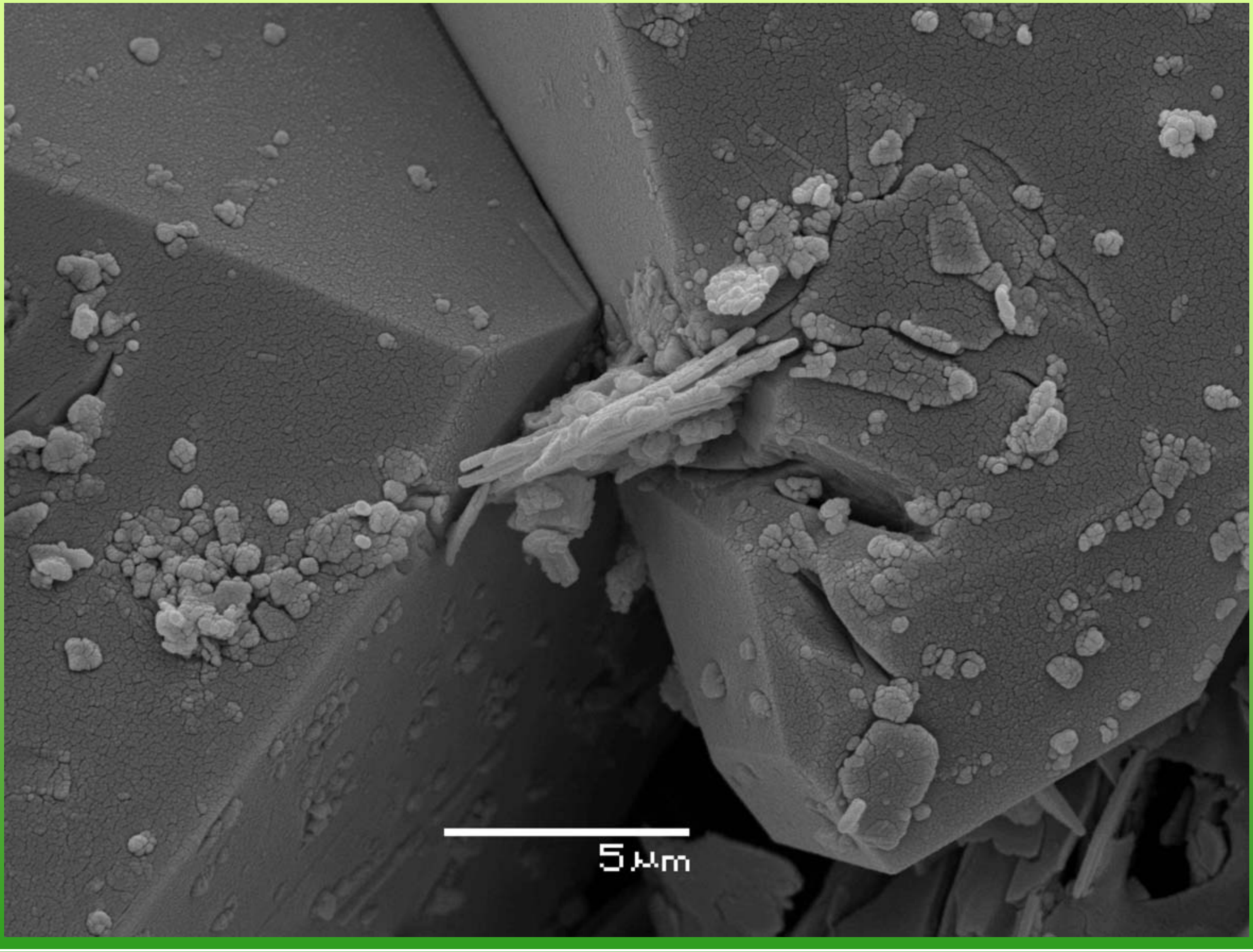
Feox reduction by hydrolysis occurs with a marked increase in alkalinity and solution iron activity
(Curtis 1985)

Fe transfered from oxides/hydroxides to carbonates, sheet silicates (chlorite, Fe-illite)

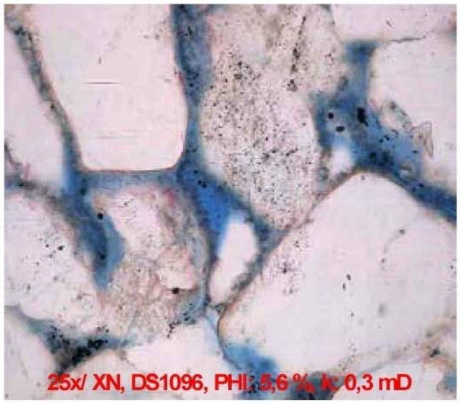
Fibrous illite with thin bitumen coating



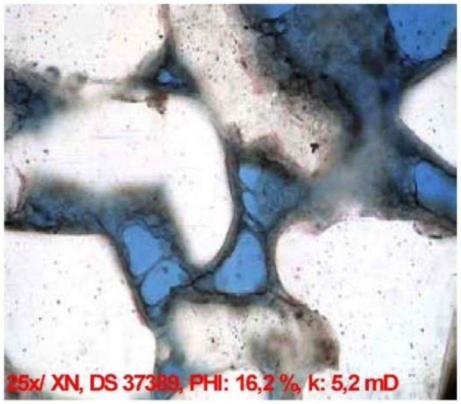
Bitumen coats on authigenic quartz and chlorite



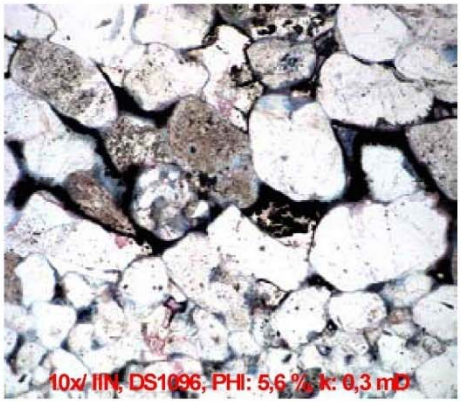
Bitumen types



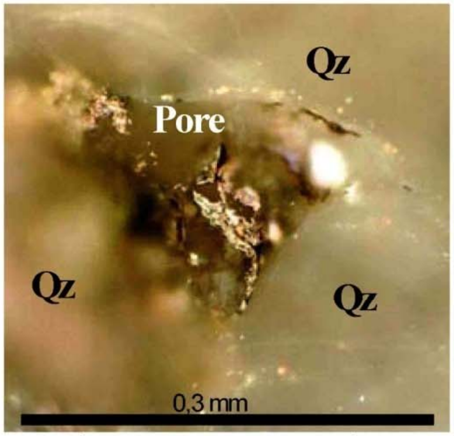
Bitumen type B1: Thin veils



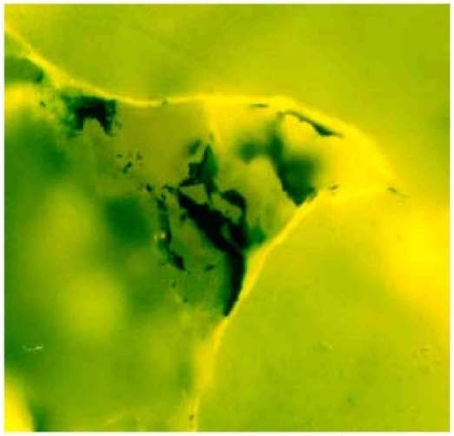
Bitumen type B2: Impregnation by clay minerals



Bitumen type B3: Solid bitumen in pores

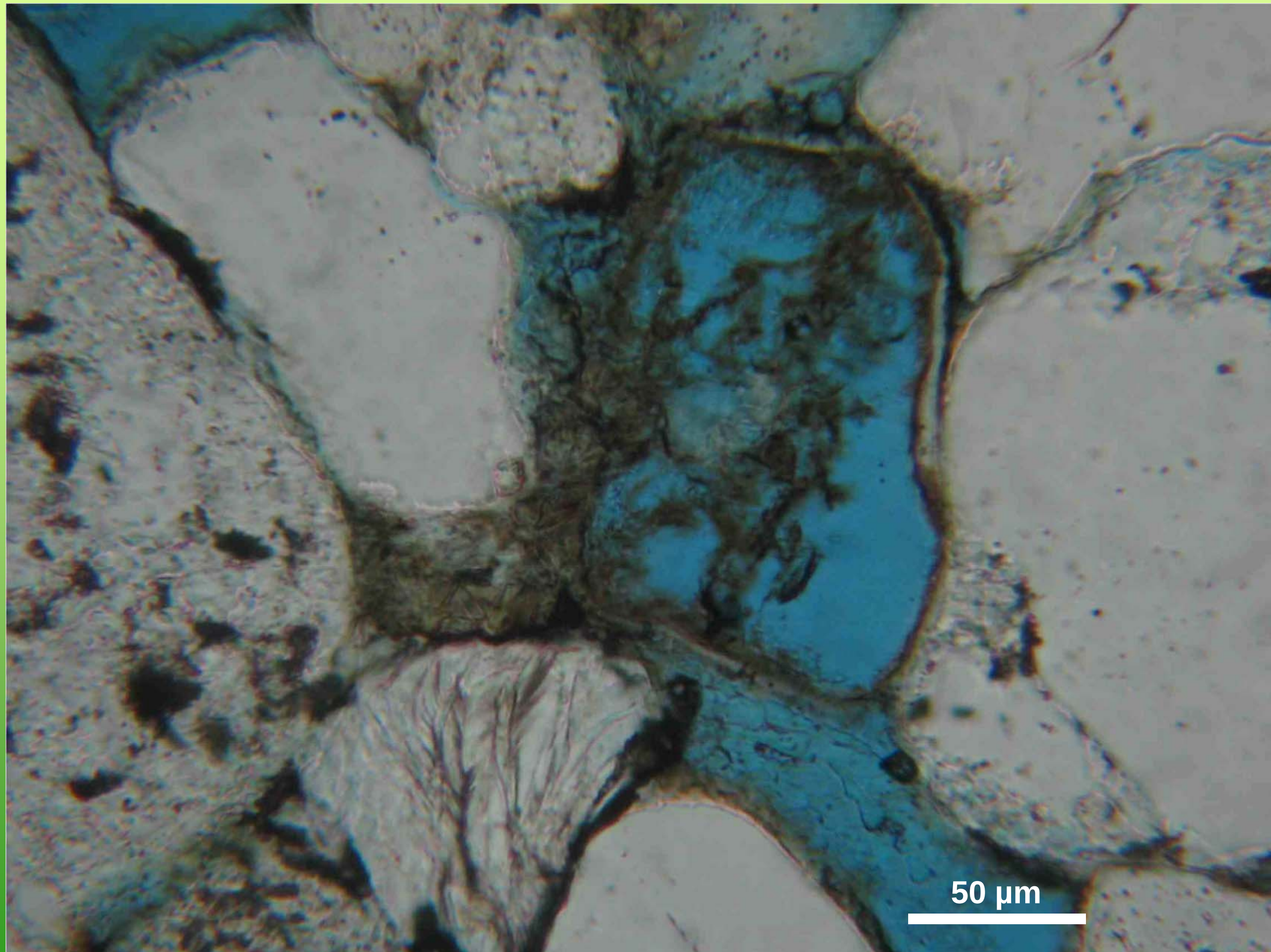


Incident light microscopy

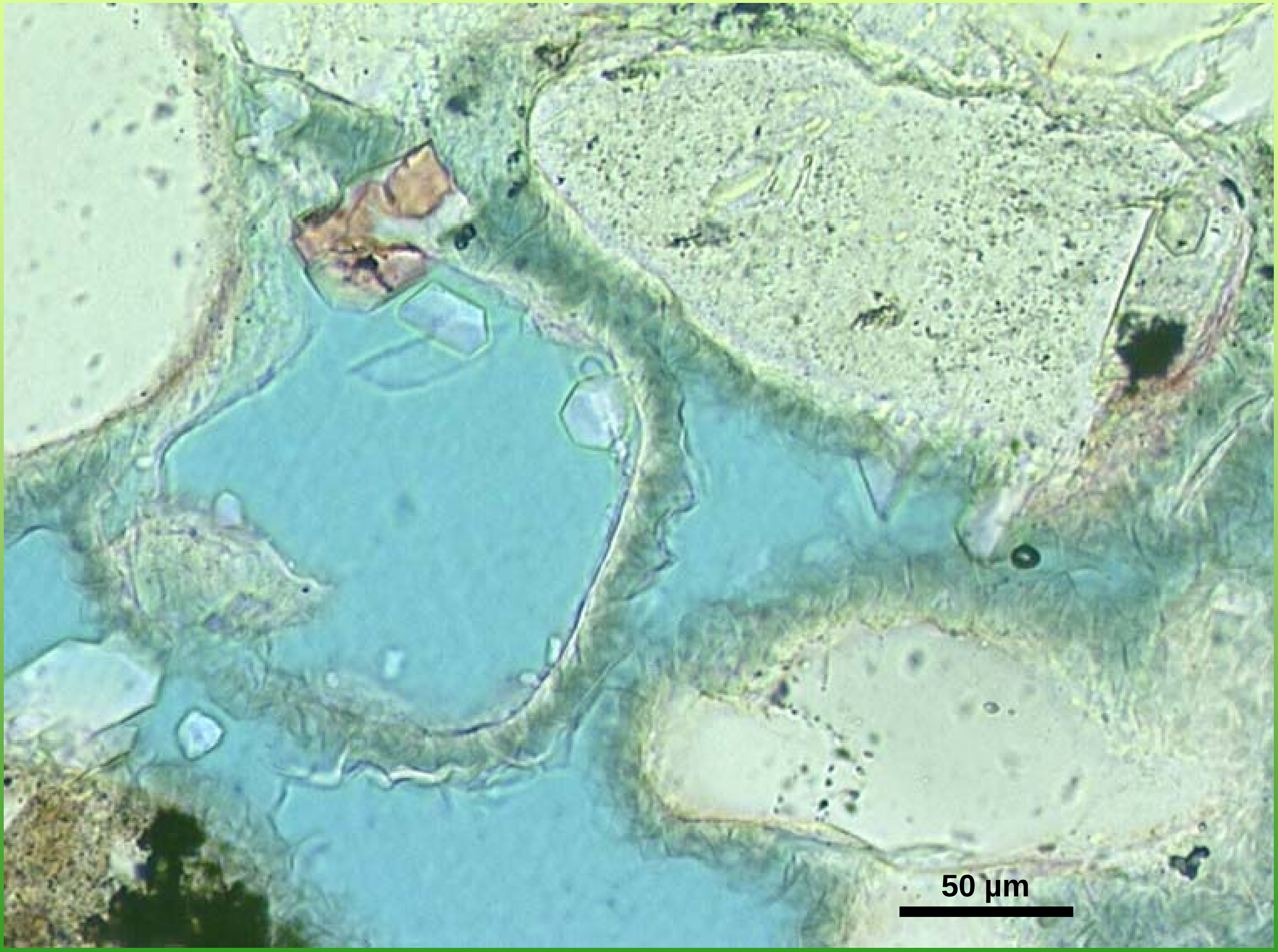


Fluorescence

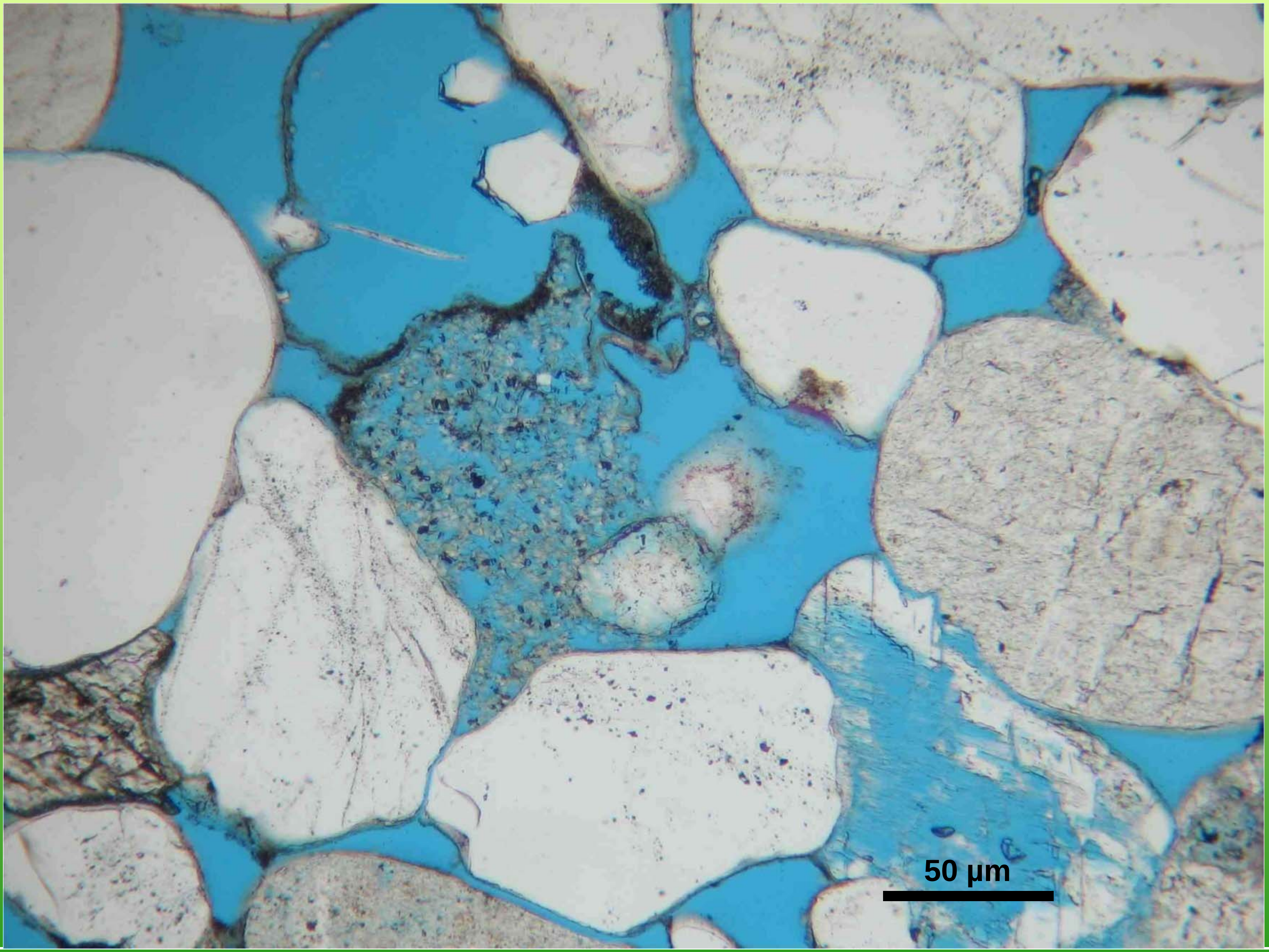
Bleaching succeeded by clay and hydrocarbons



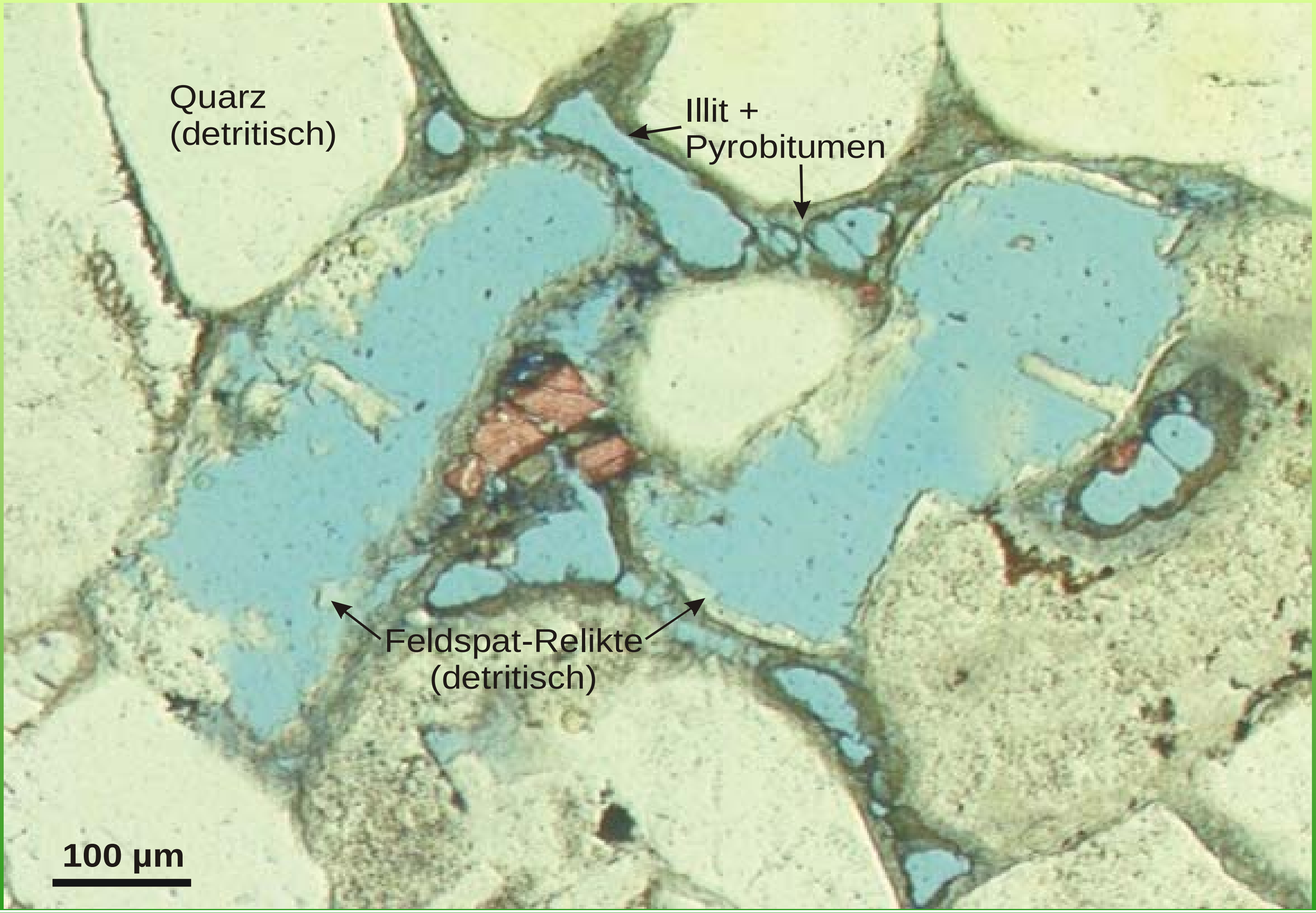
Late dissolution of clasts



Late dissolution of clasts

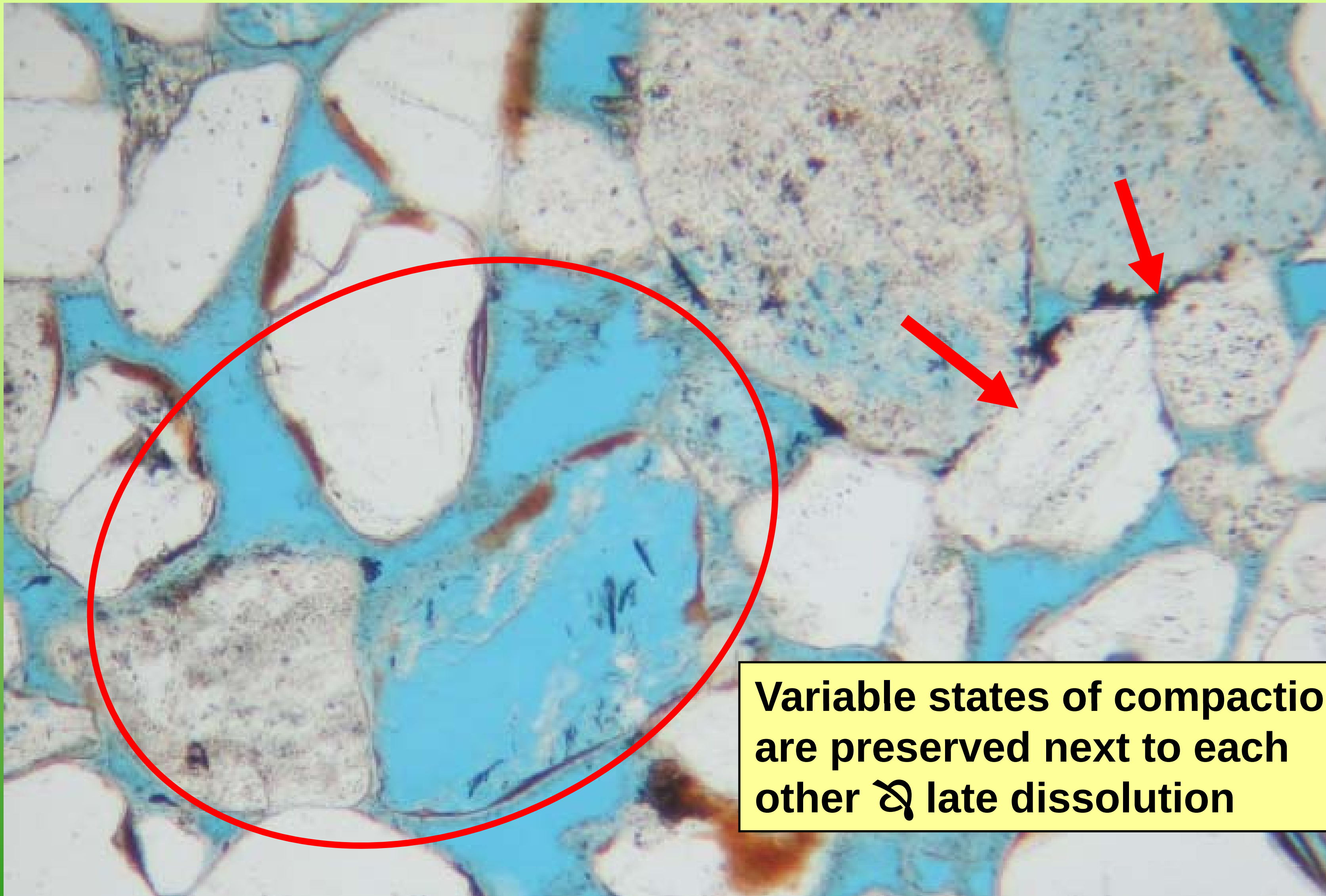


Late dissolution of clasts



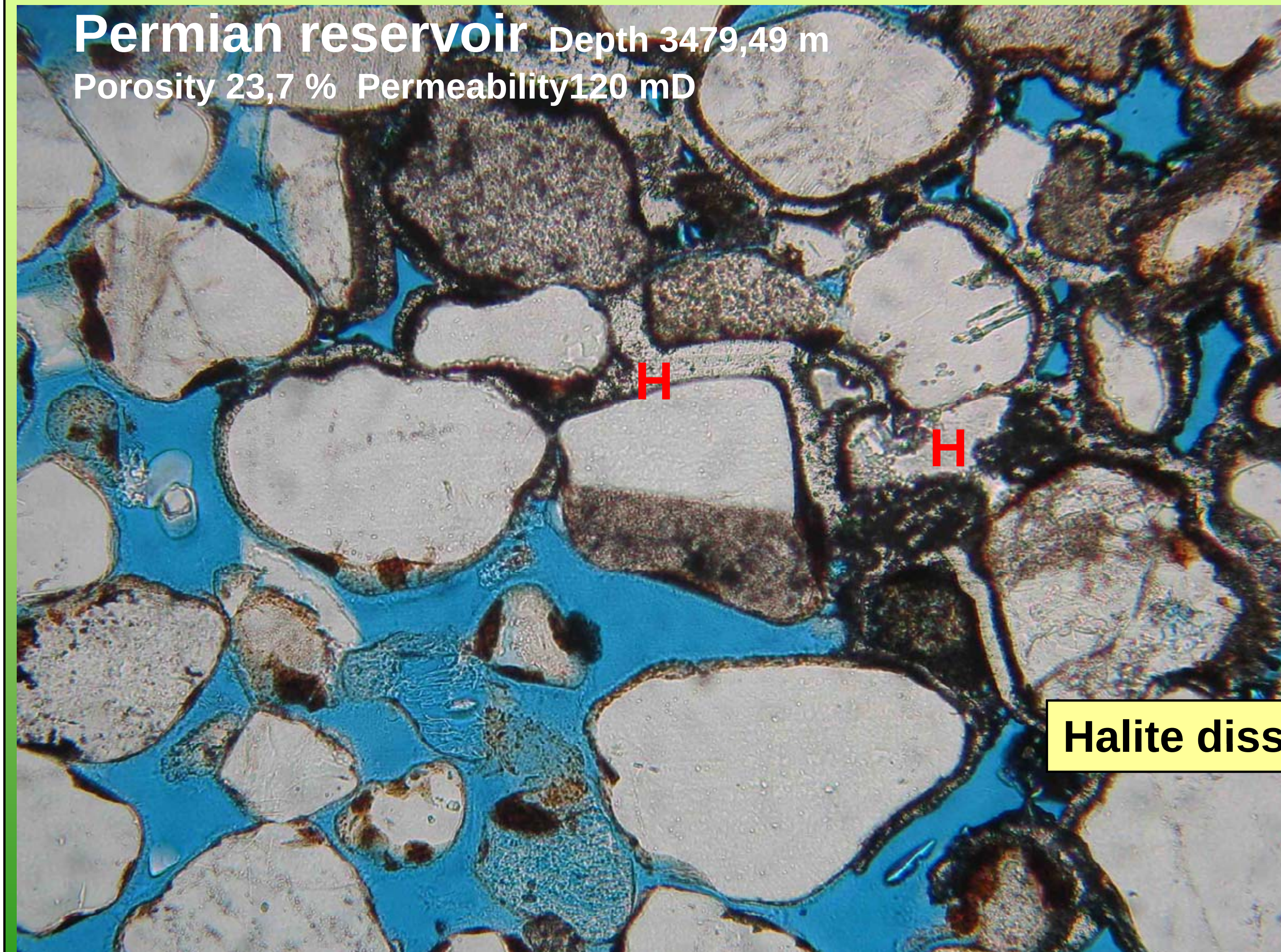
Late dissolution of clasts

Late dissolution of blocky cements



Variable states of compaction are preserved next to each other ⇨ late dissolution

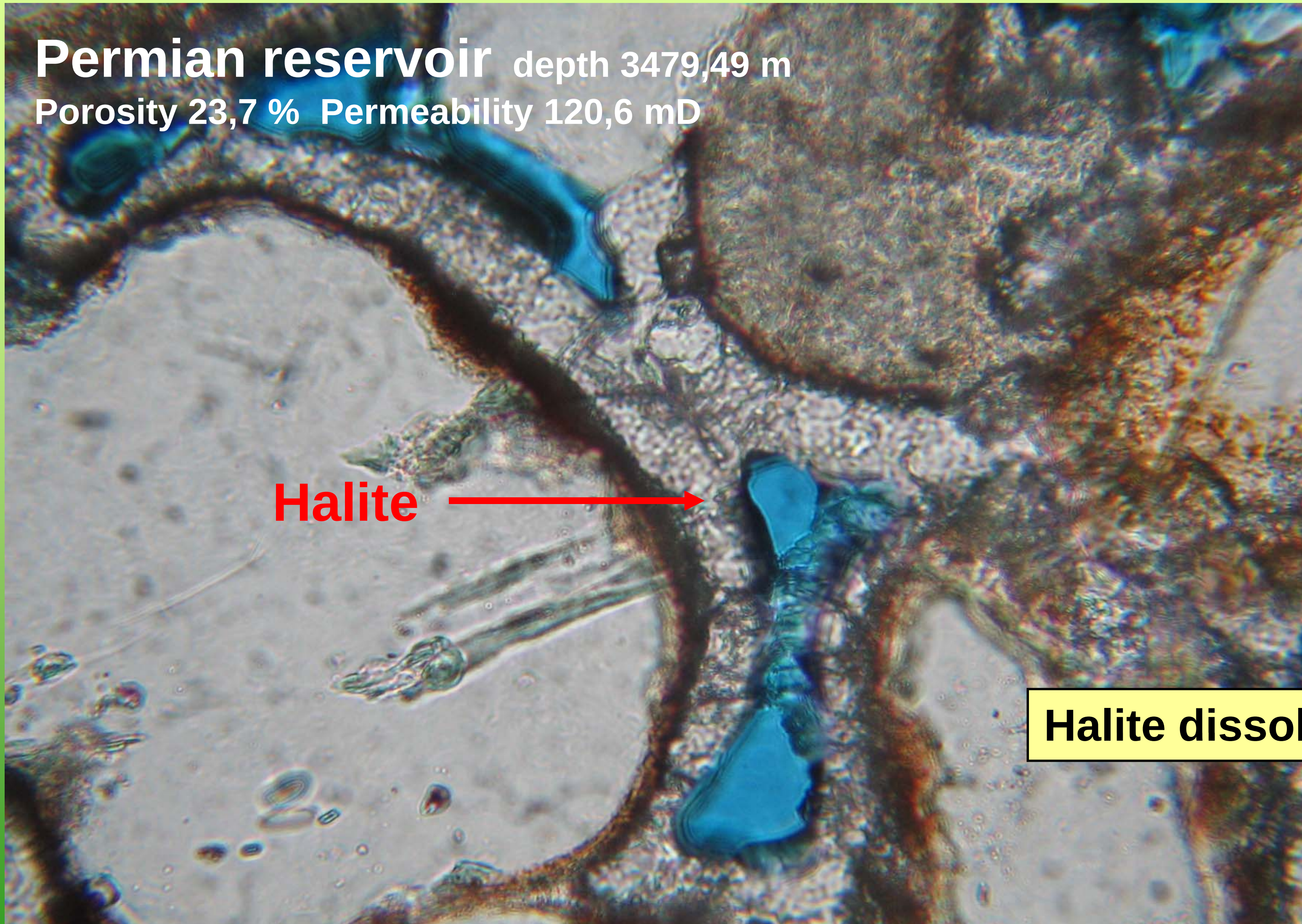
Late dissolution of blocky cements



Halite dissolution

250 µm

Late dissolution of blocky cements



Late stage dissolution of clasts and cements

Dissolution is post-bitumen

In depths of > ca. 2,5km

Clasts: feldspar, volcaniclasts, cherts

Blocky cements: carbonates, anhydrite, halite

Porosity enhancement: + 2 to 15%, averages 3 to 10%

What caused dissolution??

Elements of a Concept

Recurrent patterns:

1. Partial or total bleaching in red beds

2. (First) mesodiagenetic phase of clay growth

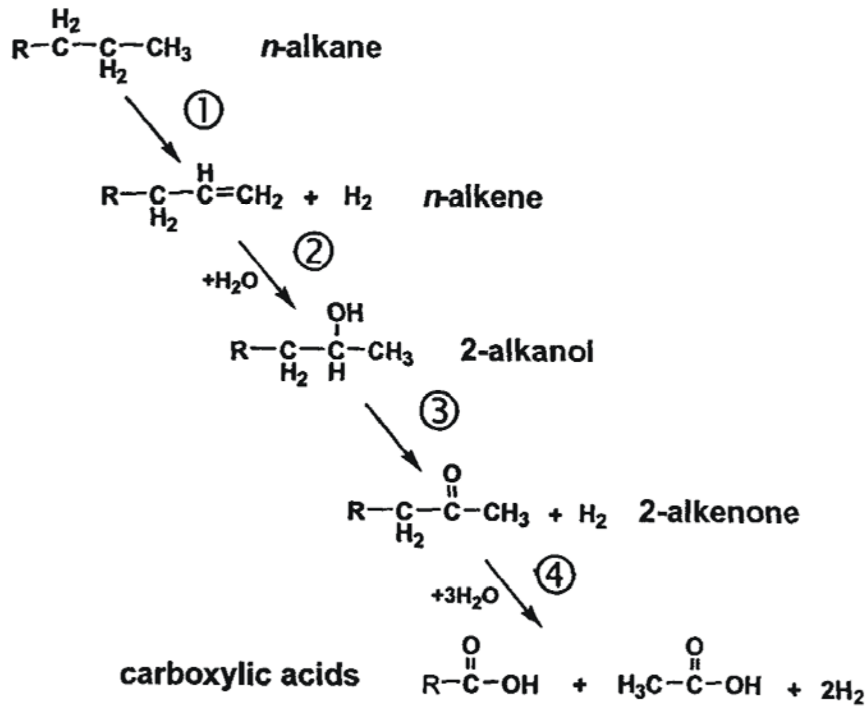
3. Oil impregnation (today as bitumen)

4. Post-oil (late stage) porosity enhancement

All these phenomena are missing in reservoirs that had no hydraulic contact to maturing source rocks.

Elements of a Concept

Seewald (2003): n-alkanes oxidize stepwise to form carboxylic acids



Seewald (2003) suggests that water and minerals from the host rock are a source of hydrogen and oxygen during organic-inorganic reactions in the pore space of clastic reservoir rocks and that the generation of reductive organic fluids may occur before, during ,and after the main stage of petroleum generation.

Elements of a Concept

Thermal alteration of oil in reservoir releases n-alkanes to the porewater

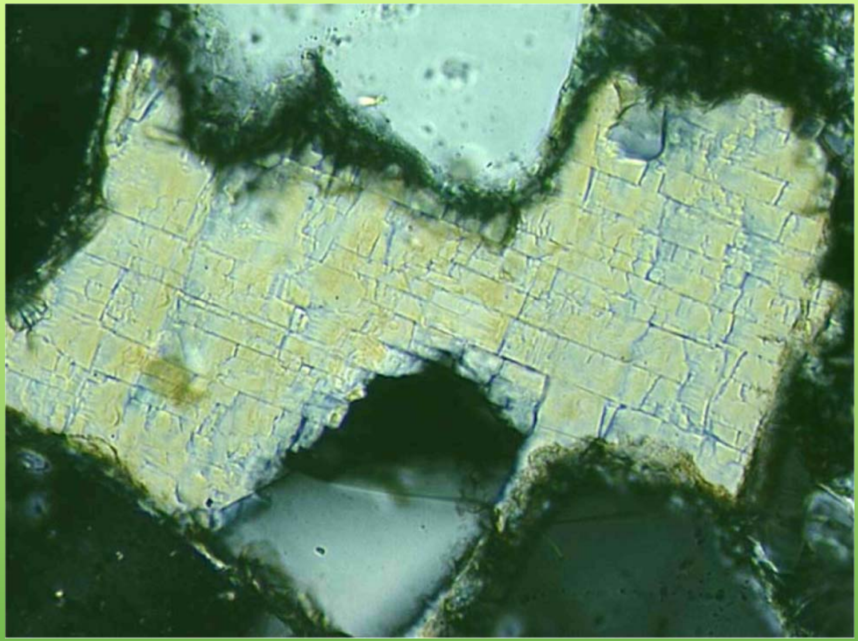
Oxidation of n-alkanes is fascilitated by close vicinity of bleached and unbleached facies

Generation of carboxylic acids within reservoirs at T >100°C allows dissolution of cements and clasts

All these phenomena are missing in reservoirs that had no hydraulic contact to maturing source rocks.

Elements of a Concept

Where is the dissolved material?

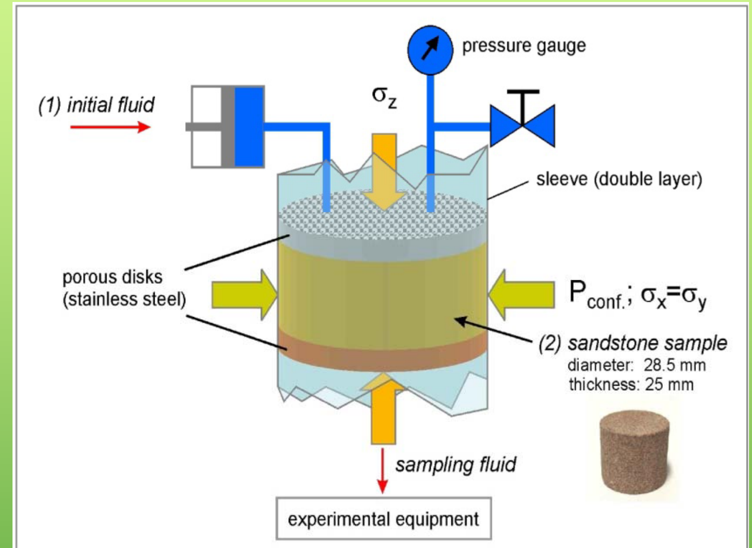


Mass balance calculation show only minor reprecipitation of dissolved material

→ net plus of stabilized porosity

Flow Cell Experiments of organic compounds in clastic reservoir rocks

Meier et al.
(2008)



Summary

1. Recurrent diagenetic phenomena in gas reservoirs, that experienced **former oil** immigration / fill

2. Bleaching–Clay growth–Bitumen and **late Enhanced Porosity**

3. Oxidation of n-alkanes from former oil leads to generation of **carboxylic acids within reservoirs at T >100°C**. Acids allow dissolution of cements and clasts

All these phenomena are missing in reservoirs that had no hydraulic contact to maturing source rocks.

Thank you for your attention

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