Recycling of sequestrated CO_2 by microbial-biogeochemical transformation in the deep subsurface

RECOBIO

Autoclave experiments – system CO_2/ autochthonic biocenosis/ formation water/ rock material for Upper Carboniferous sandstones of NW-Germany

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DGFZ

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➢ Introduction

Basic concepts of CO_2 storage (e.g. Hitchon [1996])

⇒ **Fluiddynamic trapping** (depleted gas reservoirs – EGR)

⇒ **Solubility trapping** (depleted oil reservoirs – EOR)

⇒ **Mineral trapping** (saline aquifers - Carbonates)

⇒ **Coal bed methane** (coal seams - ECBM)

- **Fluiddynamic-geochemical point of view**

But also question of biogeochemical transformation

⇒ **CO_2 - electron acceptor, carbon source**

⇒ **Biogeochemical CO_2-reduction (CH_4/ H_2S- formation)**

⇒**Dissolution/ solid phase formation - increasing storage capacity**

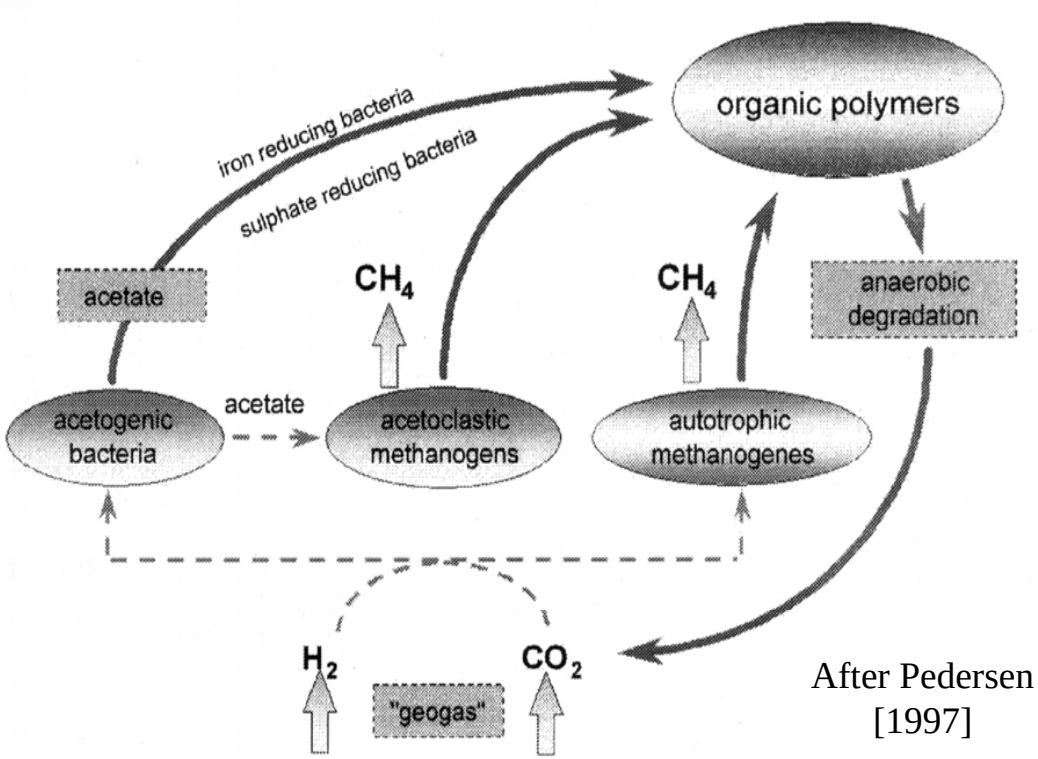
➢ Importance deep biosphere

Bak, Kleinitz, Widdel (1980`s to 1990`s)

- **Impact of SRB on oil production, gas storage (scale, H_2S, corrosion)**

***Kotelnikova (2002)* ⇒ comprehensive literature review**

- **Importance of methanogenic microbes (last decade)**



After Pedersen [1997]

- **Autotrophic pathway ⇒ CO_2-reduction**
- **Acetoclastic pathway ⇒ Net CO_2-reduction by incomplete fermentation**
- **Competition, symbiosis ⇒ Fe- and SO_4 reduction**

Main question ⇒ H_2 *in situ* supply

➢ Main RECOBIO objectives

1 Characterisation of the autochthonic microbial biocenosis

⇒ **evidence of autotrophic (CO_2 fixing) microorganisms**

⇒ **Understanding Metabolisms (Cultivation independent methods)**

2 Mechanisms of H_2 in situ supply

⇒ **evidence of *insitu* supply**

⇒ **test of relevant minerals/ rocks**

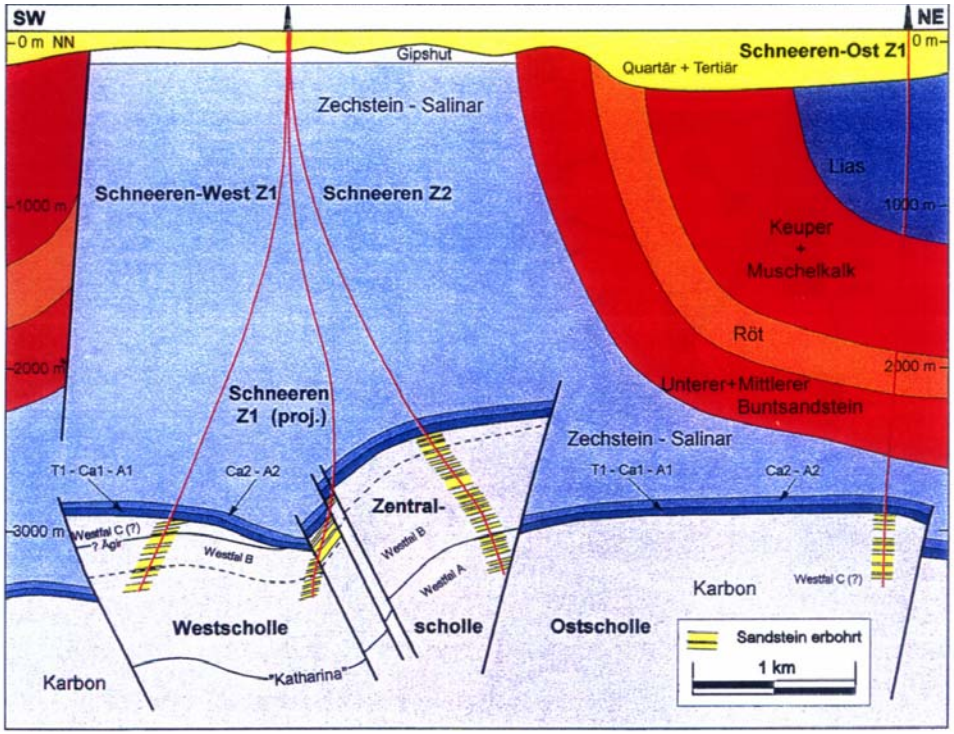
3 Autoclave experiments - Biogeochemical transformation

⇒ **Use of autochthonic biocenosis**

⇒ **System: produced formation waters, rock material, CO_2/H_2-gas phase**

⇒ **Near to "real world",**
but speed up (H_2), sampling (rock-water ratio), handling (10 bar)

➢Gas field site Schneeren



from Hollmann et al. [1998]

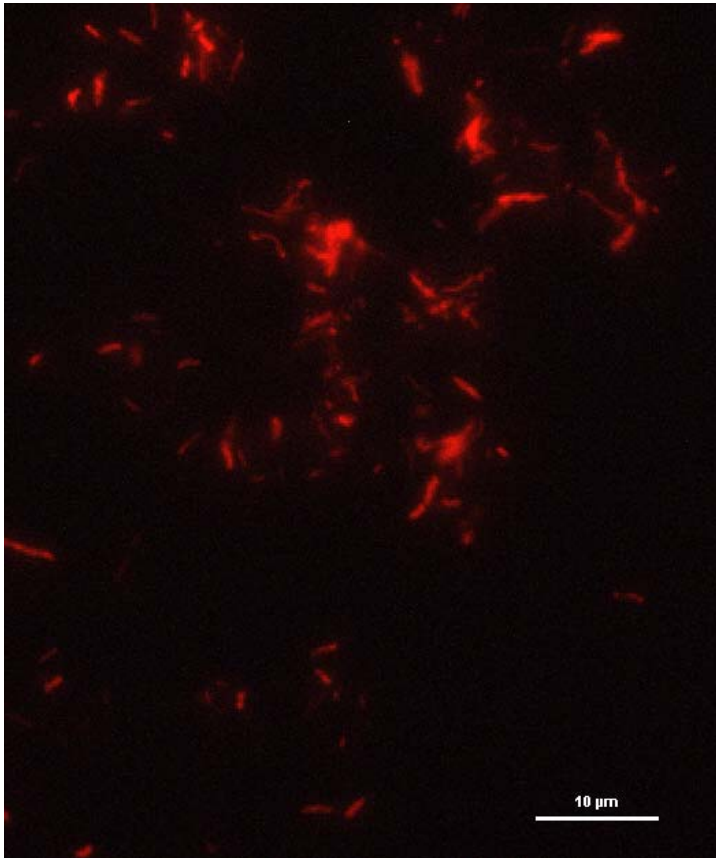
⇒ **Compacted Wesfal-C sandstones (Upper Carboniferous)**

⇒ **Subsalinar horst-structure, natural fractured**

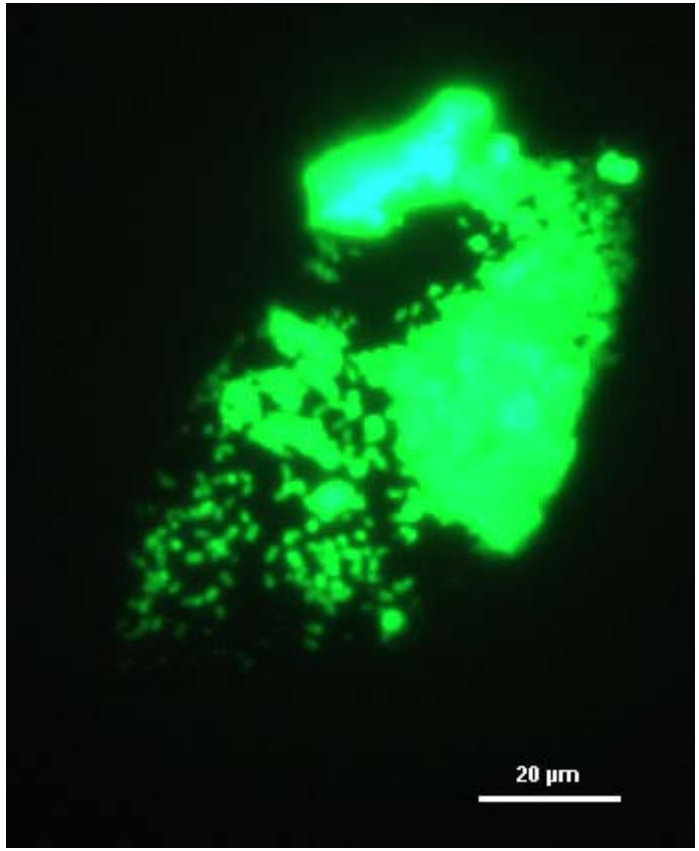
⇒ **Field was opened in the late 1980`s**

⇒ **Temp. 80 to 90°C, salinity up to 250 g/l, > 2300 m deep**

➢A1) Gas field Schneeren – autochthonic biocenosis



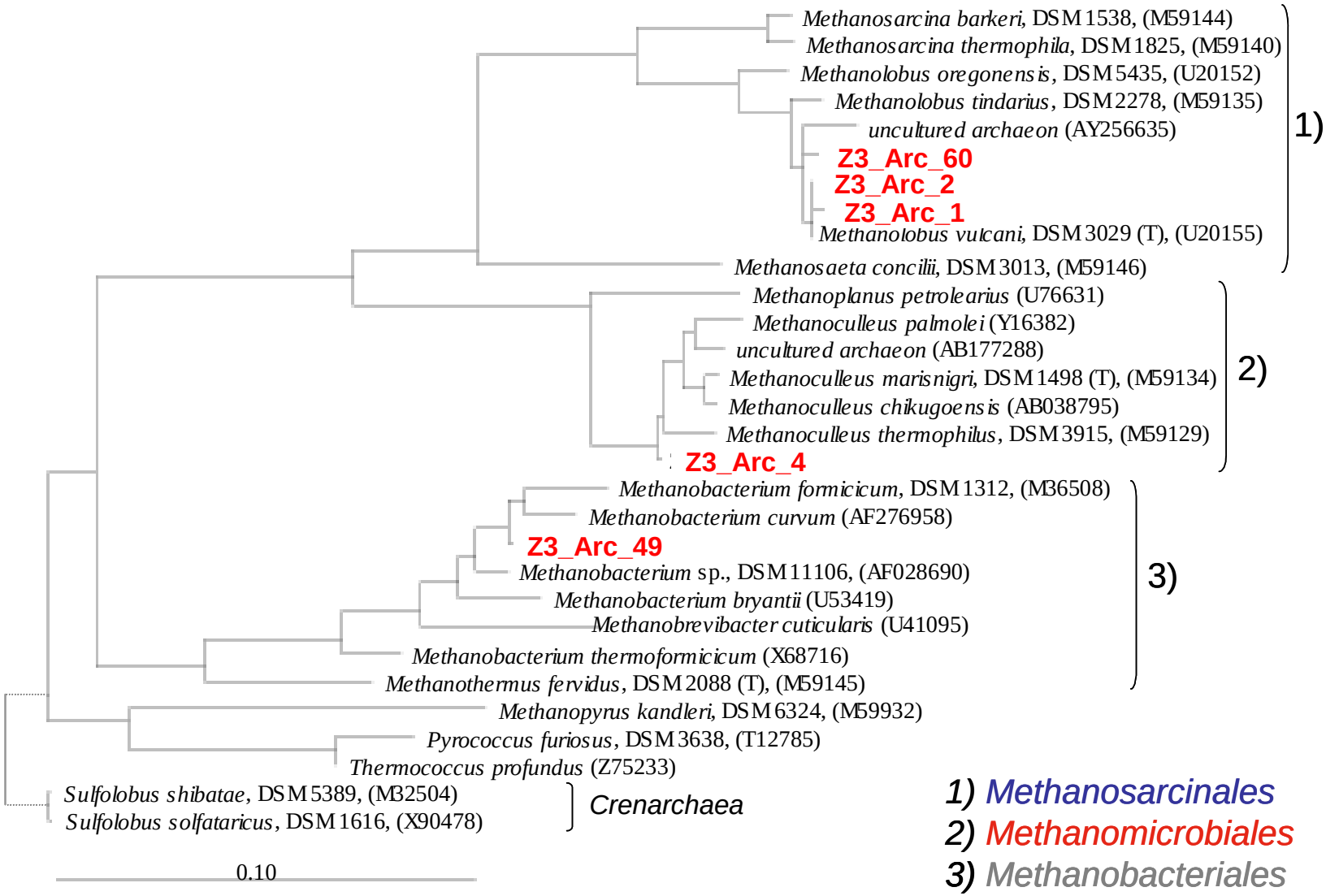
- borehole Z3 - *Bacteria*



- borehole OstZ2 - *Archaea*

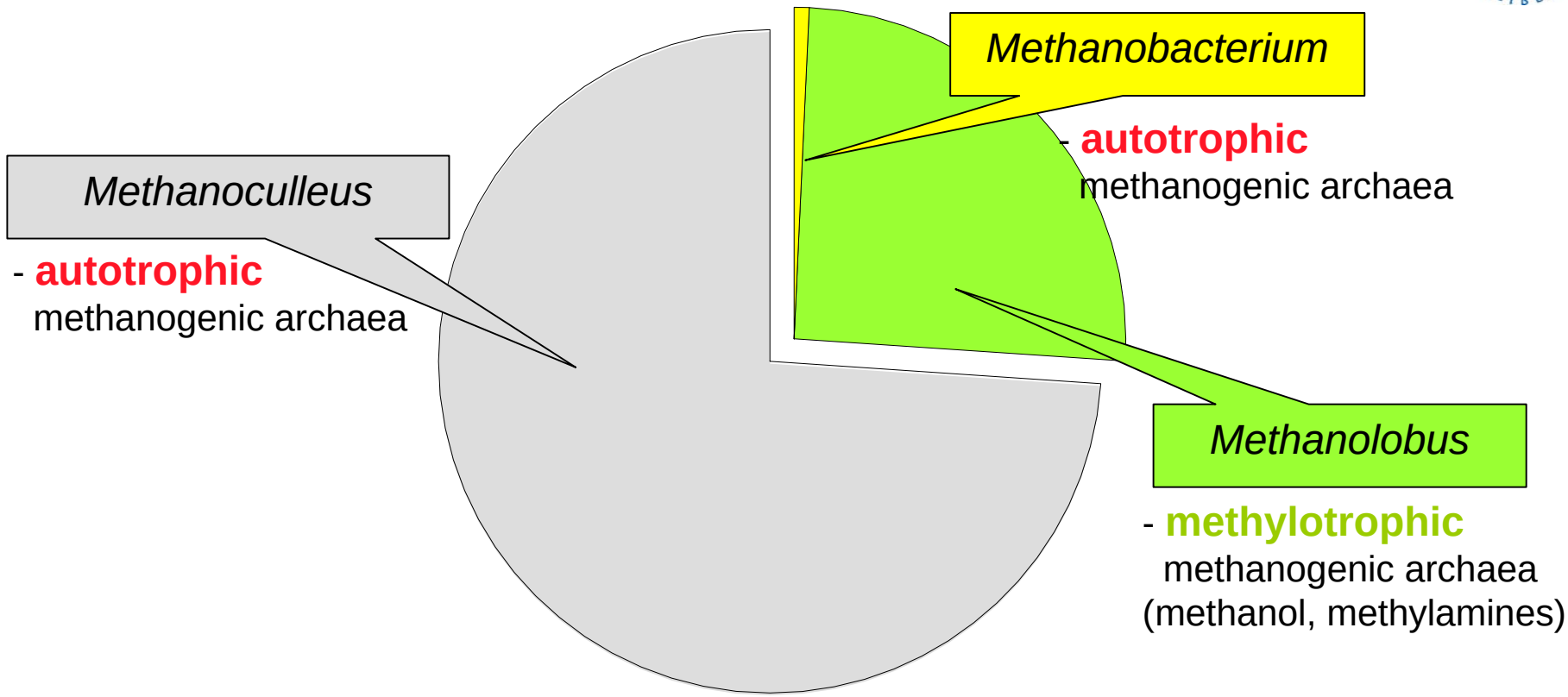
⇒ **investigation by FISH (Fluorescence in situ hybridization) at produced formation waters**

➢A1) Gas field Schneeren – Archaea



1) Methanosarcinales
2) Methanomicrobiales
3) Methanobacteriales

➢A1) Gas field Schneeren – Archaea



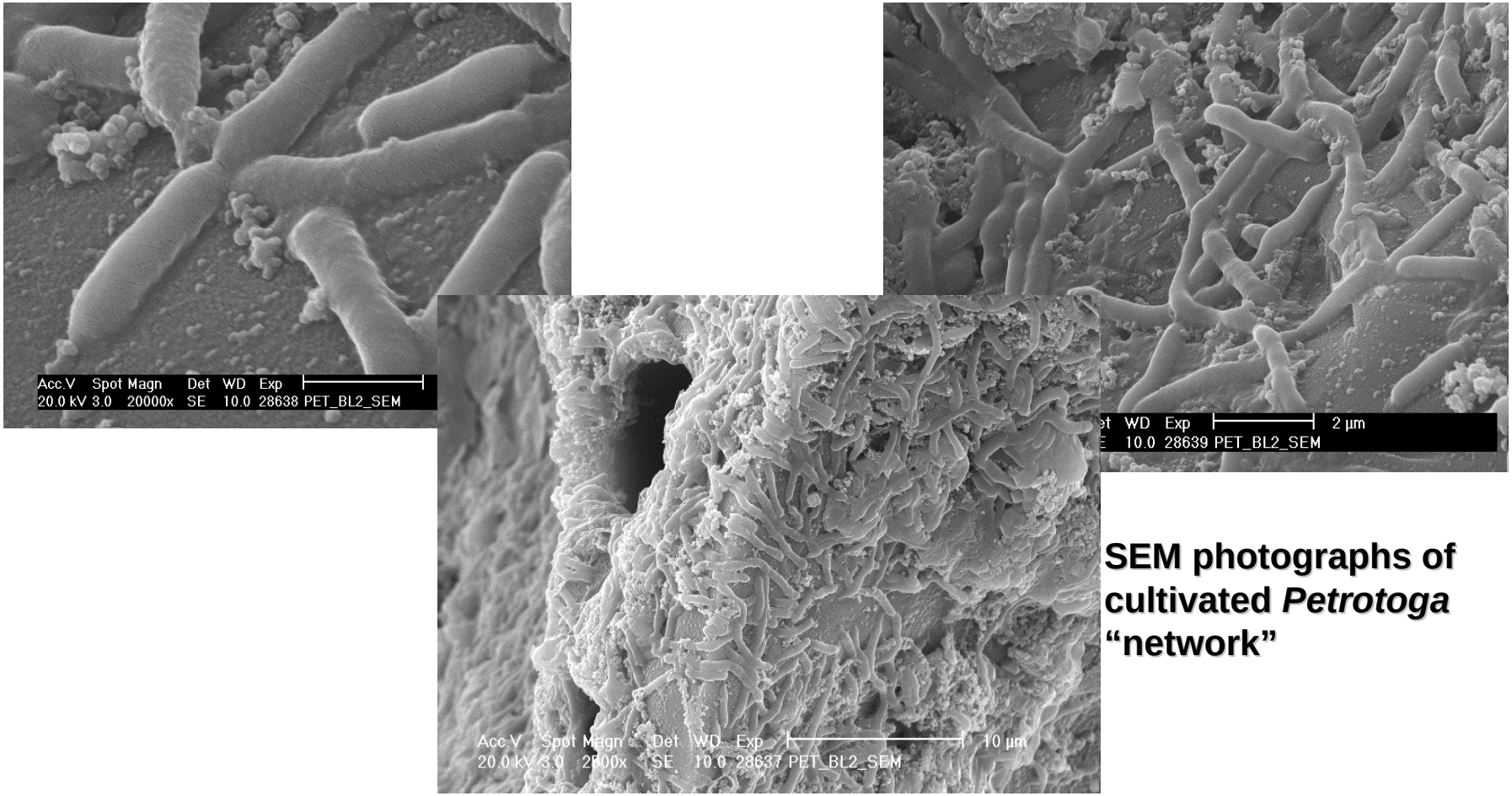
⇒**All Archaea are methanogenic**

⇒**There are autotrophic (CO_2-fixing) and heterotrophic (C_{org} – degradation) metabolism present**

➢A1) Gas field Schneeren – Bacteria

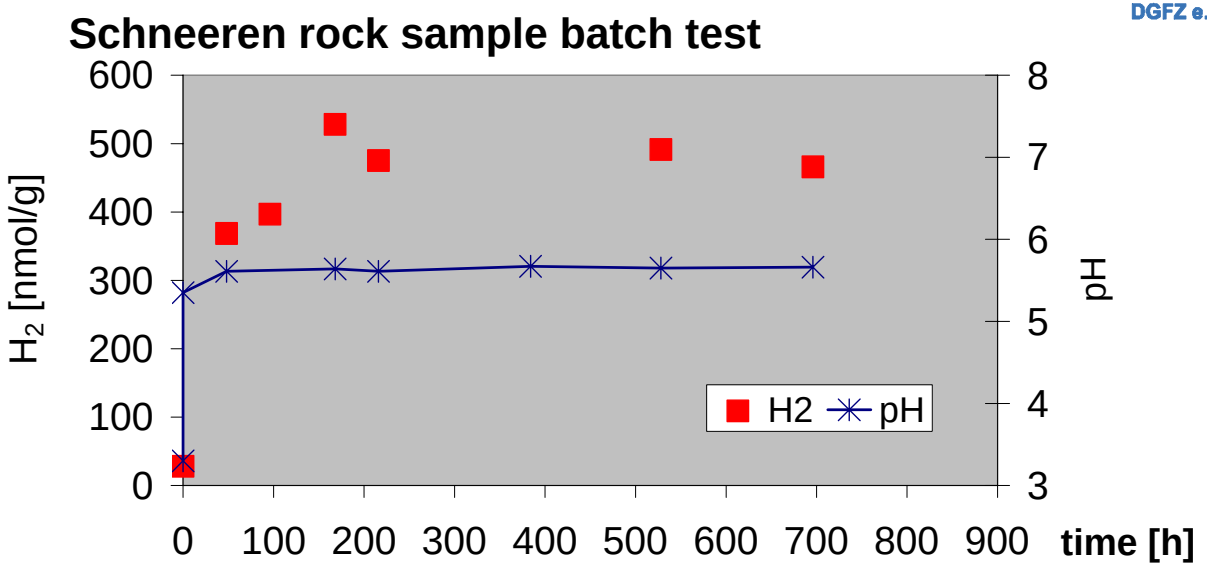
⇒**Main species: fermenting and CO_2 fixing, SO_4-reducing Bacteria**

⇒***Petrotoga, Thermoanaerobacterium* and *Desulfotomaculum***



SEM photographs of cultivated *Petrotoga* "network"

➢A2) *insitu* H_2-supply



⇒H_2 supply shown for different relevant minerals and the formation rocks

⇒Continuous release as equilibrium between solid and fluid phase

⇒Fe-content of minerals/ rocks important up to 0,1 Ma%

⇒More important organic complexation of rock surface

➢A3) Autoclave Experiments - Equipment

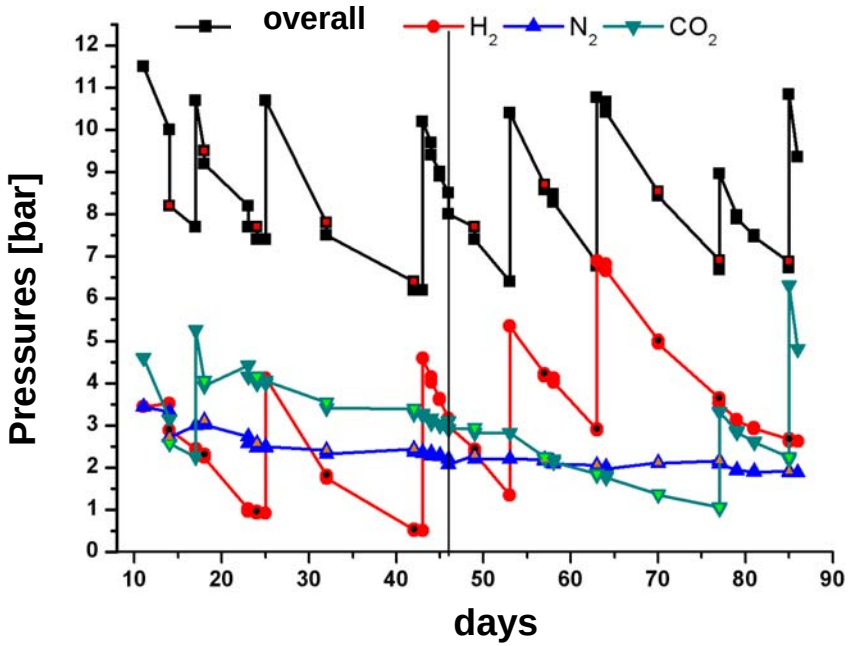
Autoclaves/ GC

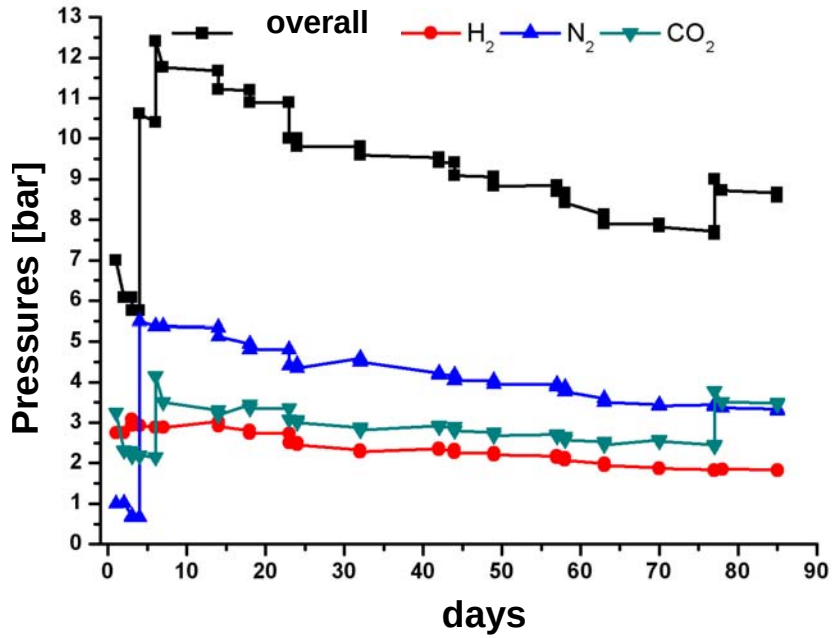
- Total volume (500/ 200 ml)
- Online GC-TCD, T_{reac}, p_{reac},T_{out}
- Gas and liquid sample port

Experimental System

- Prod. Form. Waters with MO, milled rocks, CO_2/H_2-Gas Phase
- Ratio rock/ formation water ≈ 1: 7,5
- Two parallels sterile and non-sterile
- 10 bar, 40 °C

➢ A3) Autoclave Experiments – gas phase





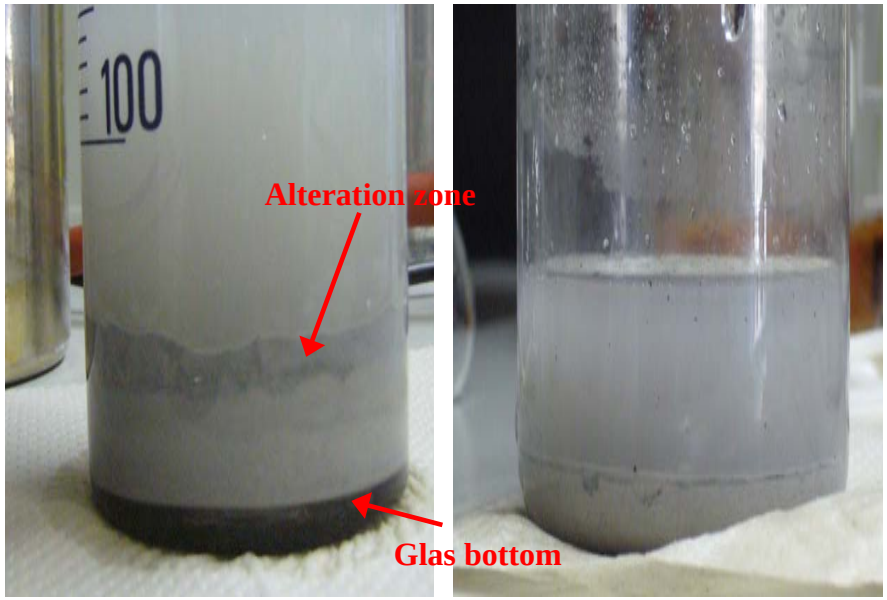
Non-sterilised (biogeochemical) test **sterilised (geochemical) test**

⇒ **Sterilised Autoclave - Pressure loss only by sampling**

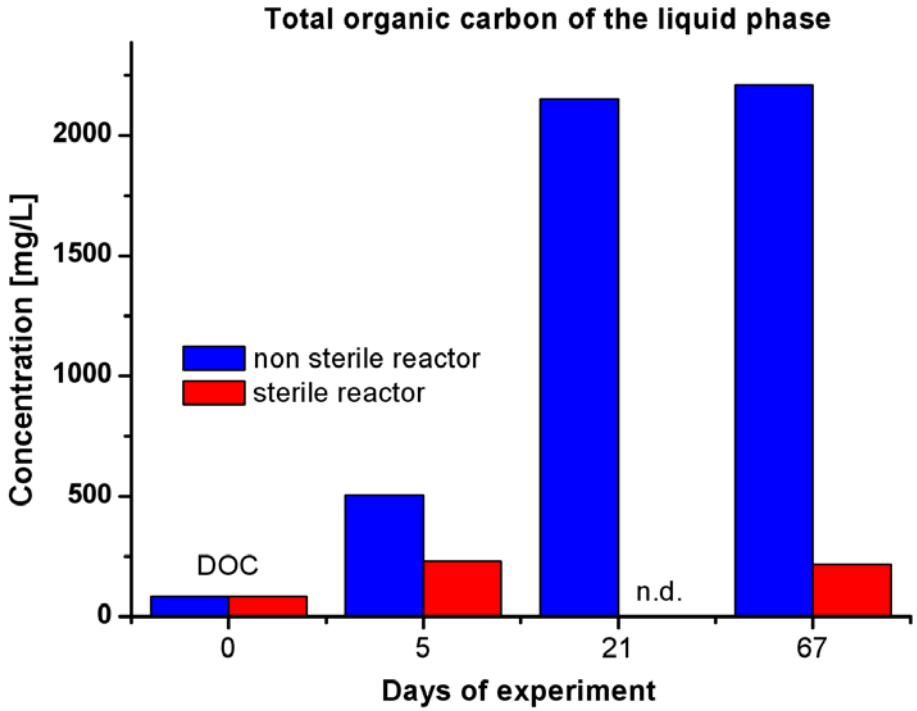
⇒ **Non-Sterilised Autoclave – fast H_2, CO_2-consumption**

⇒ **fast sulphate reduction, after 50 d starting methane formation**

➢ A3) Autoclave Experiments – liquid/ solid phase



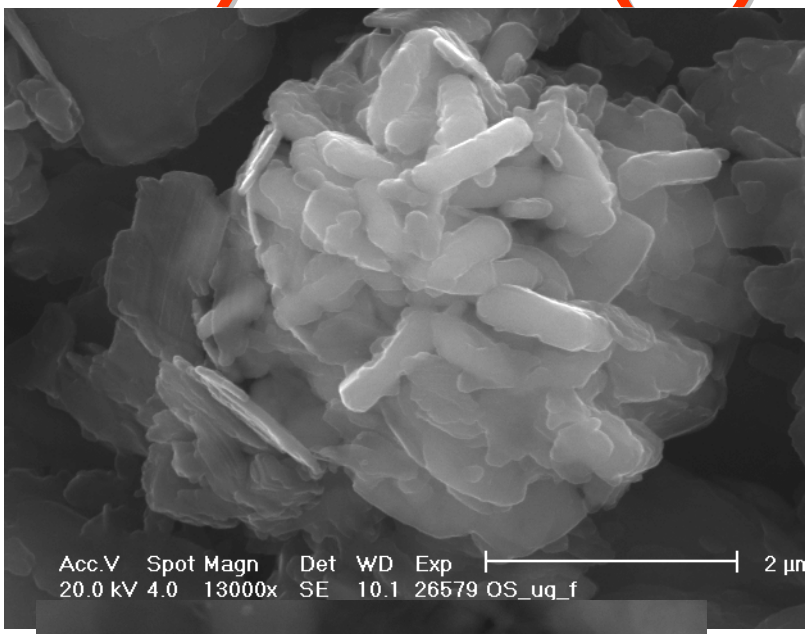
Non-sterilised test Sterilised test

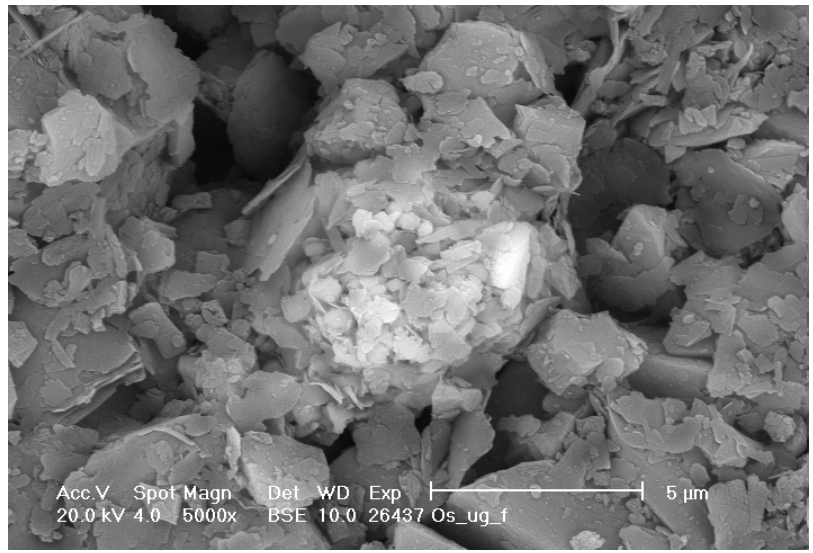


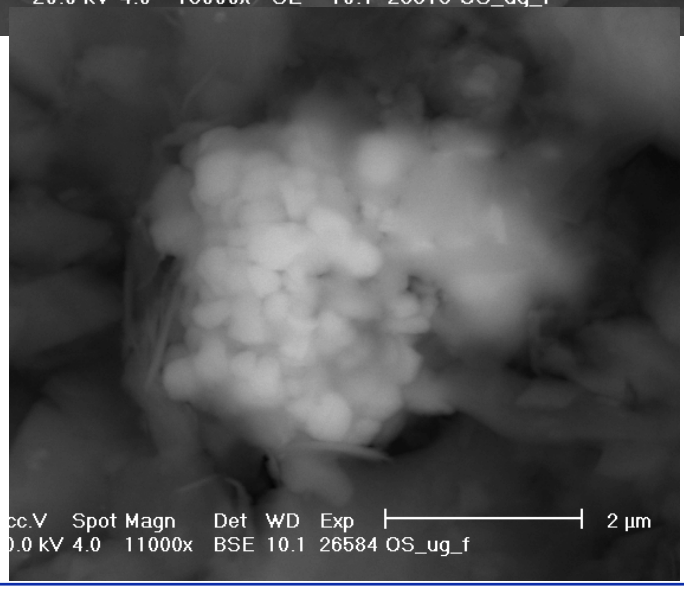
⇒ **Enrichment of TOC, TIC and red. Fe-Sulphur Phases in the alterated zone**

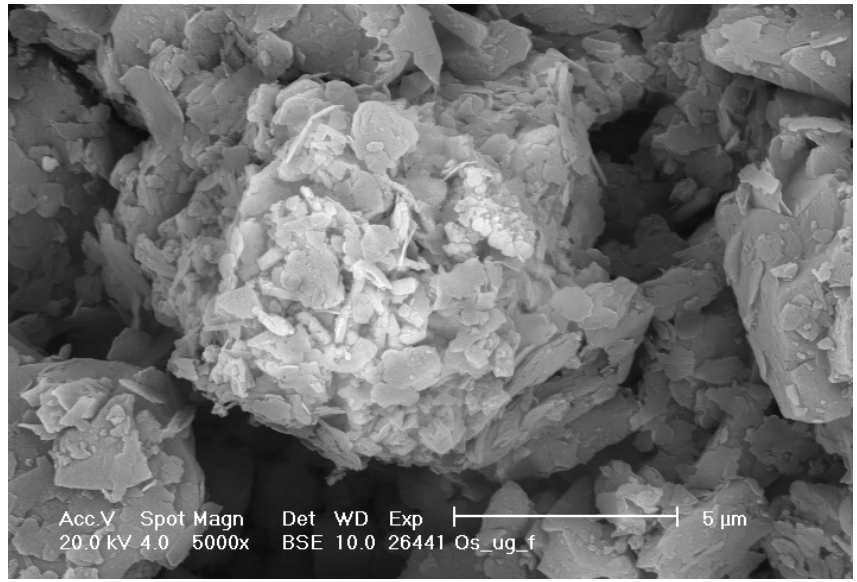
⇒ **Massive DOC increase**

➢A3) Formed (Fe)S-phases

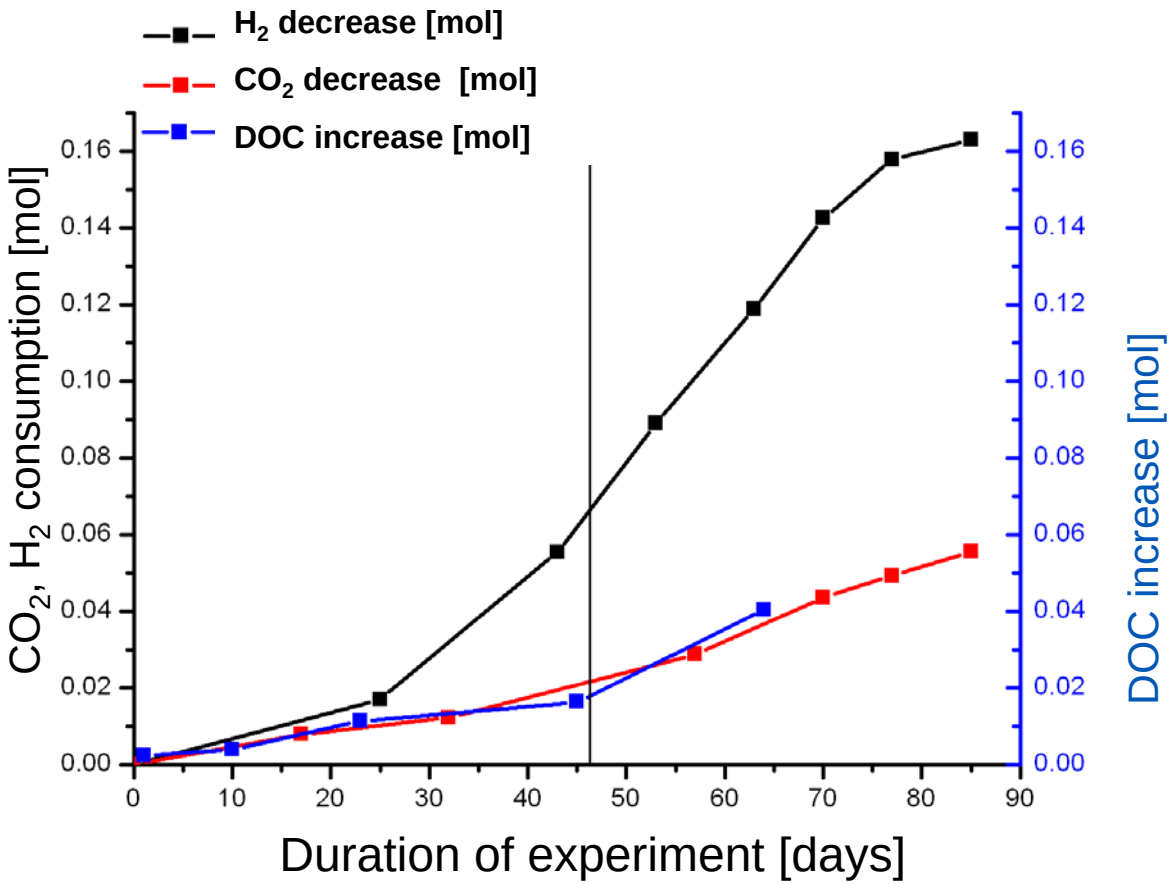








➢ DOC increase by CO_2 uptake – balance of composition

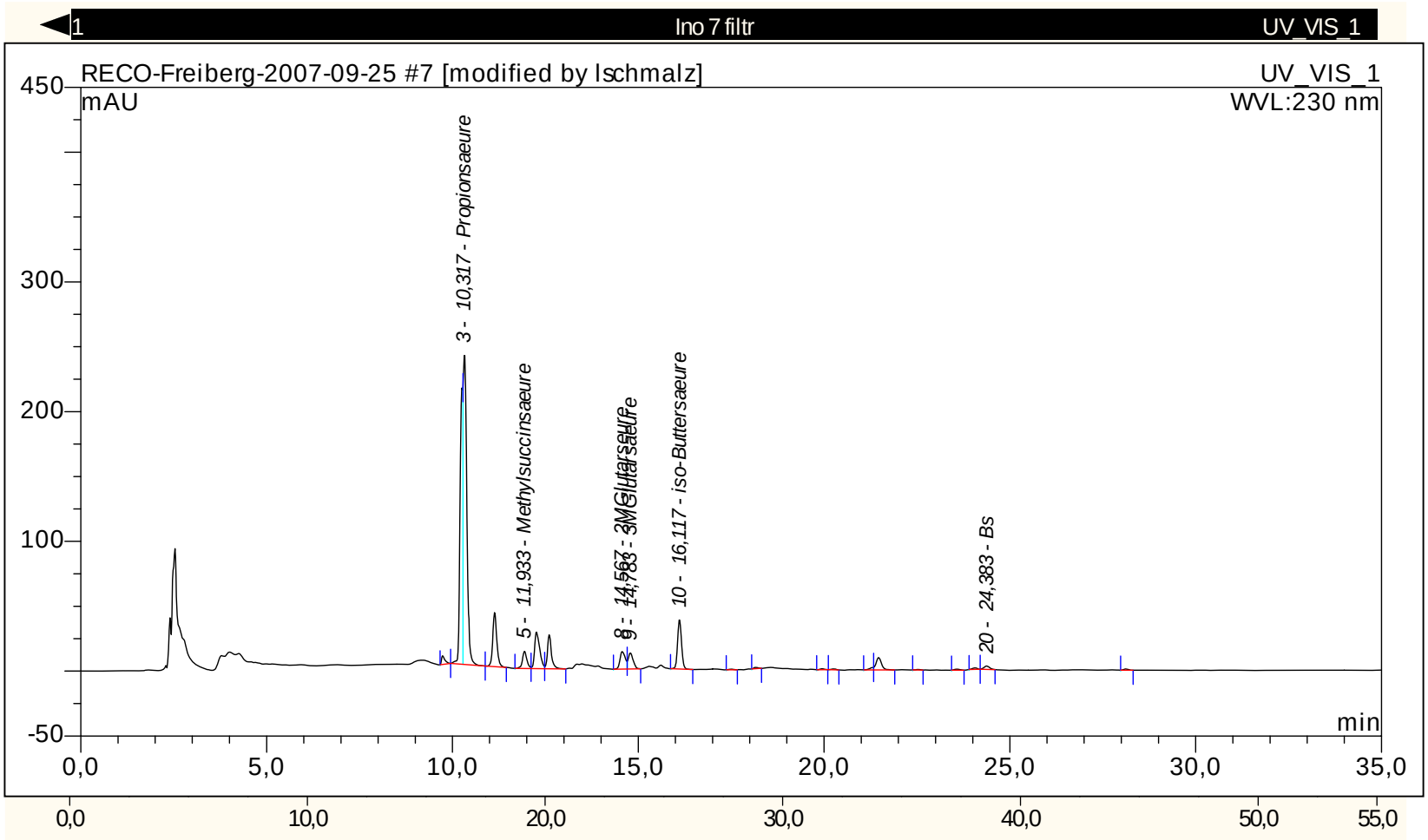


Microbial, non-sterilised autoclave

⇒ **DOC build up, can be explained by CO_2 partial pressure loss**

⇒ **LC-OCD – neutral/ amphiphilic substances and low-molecular substances**

More detailed characterisation (HPLC, GC-MS)



⇒ **Complex carbonic acids**

⇒ **Also extracellular polymeric substances (EPS) – polysugars, proteins**

⇒ **Link to town gas storage operation (1960s – 1980s)**

➢ Town gas storage operation

⇒**Build up of biomass and fatty acids, sulphate reduction (Ketzin – GDR, Engelbostel – FRG, Beynes- FRA, Lobodice – TCH)**

⇒**Town gas, mixture of H_2, CO, CH_4, N_2**

⇒**Unpublished reports 1980s - upper storage unit Ketzin, >700 mg/l decrease of sulphate (in nearly 15 years operation)**

⇒ **Postulated that up to the half of the gas pressure loss could not be explain abiogenic but by biogenic processes (build up of biomass, formation of carbonates/ sulphides)**

⇒ **Important to known and consider these biogenic processes – otherwise interpreted as leaky storage unit**

⇒ **Interesting to discuss the DOC-build up at the Frio Experiment (Texas) – talk/ paper by Kharaka et al. (USGS)**

Summary - Conclusions

➢ Conclusions/ Outlook

⇒ Evidence of autotrophic (CO_2-fixing) metabolisms

⇒ H_2-supply was shown at relevant minerals/ rocks

⇒ Sulphate reduction, DOC-build up

⇒ Important to known and consider biogeochemical processes – otherwise pressure loss interpreted as leaky storage unit

⇒ Ongoing investigation with ^{13}C-labelled CO_2

⇒ Also investigation of the Altmark Gasfield

⇒ in-situ sampling of the formation waters

⇒Question of microbial impact to carbonate phase formation

Acknowledgments

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