Microbially mediated processes in early diagenesis

Weenzen gypsum diapir

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DER FORSCHUNG | DER LEHRE | DER BILDUNG

SaltGiant Short Course 1

Modern and ancient oceans

Salamaca, November 25

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Microbially mediated processes in early diagenesis

(1) Early diagenesis – an introduction

(2) Early diagenesis in hypersaline settings

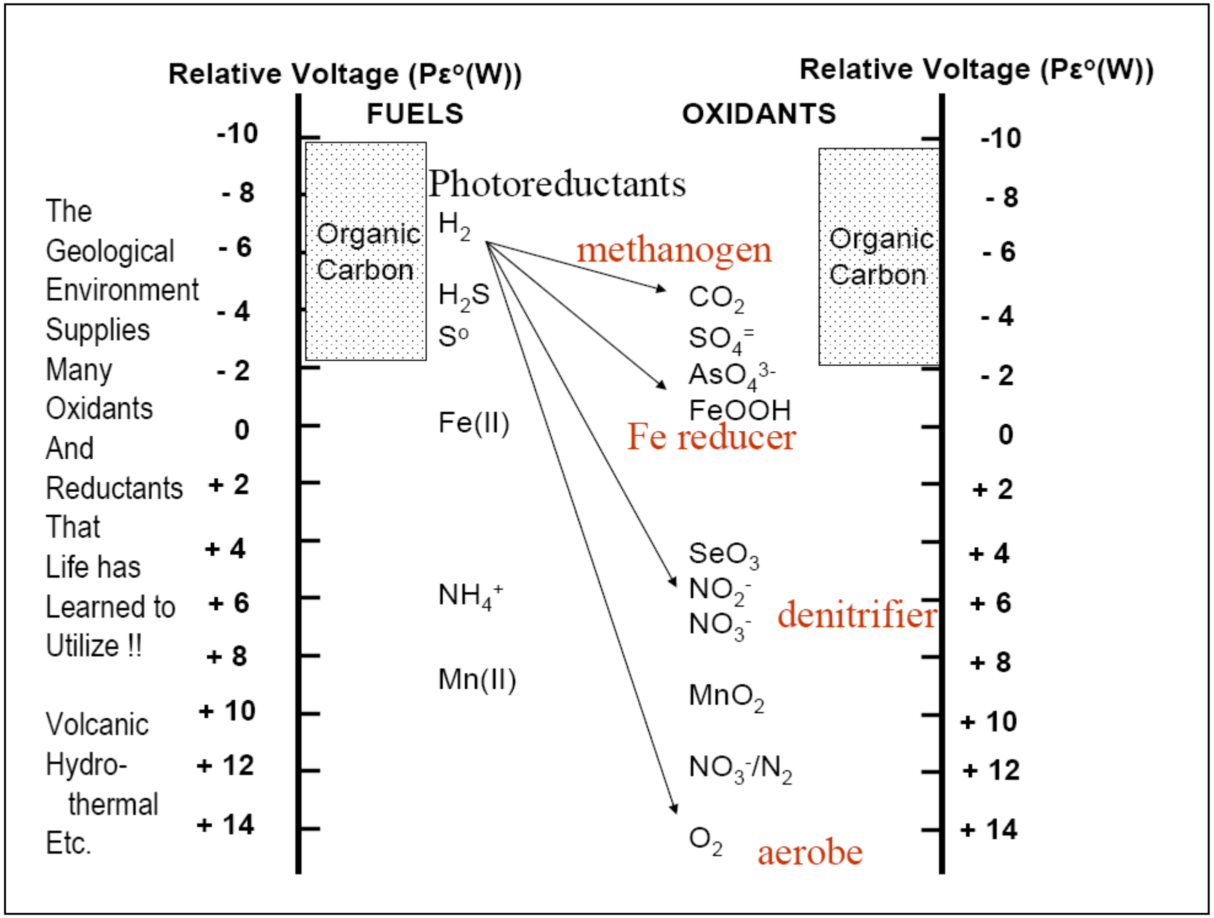
(3) Syngenetic sulfur formation

(4) Epigenetic sulfur formation

(5) The issue with sulfide oxidation in the subsurface

(6) Calcare solfifero

Early diagenesis – an introduction



Metabolism first

<u>Candidate metabolisms</u>

Methanogenesis

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$

Acetogenesis

$$2\ CO_2 + 4\ H_2 \rightarrow CH_3COOH + 2H_2O$$

Berner (1981) subdivided sediments into oxic and anoxic. Anoxic sediments are subdiveded into sulfidic and non-sulfidic. Anoxic non-sulfidic sediments are further subdivided into suboxic and methanic.

Diagenetic zones are defined by the utilization of organic matter by variable microbial communities. Their distribution is determined by the energy yields of the respective biogeochemical reactions.

Reaction	DG° (KJ mol^{-1} of CH_2O)
Oxic respiration:	
$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-475
Denitrification:	
$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	-448
Mn-oxide reduction:	
$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-$	-349
Fe-oxide reduction:	
$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$	-114
Sulfate reduction:	
$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	-77
Methane production:	
$2CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2$ and	
$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O^b$	-58

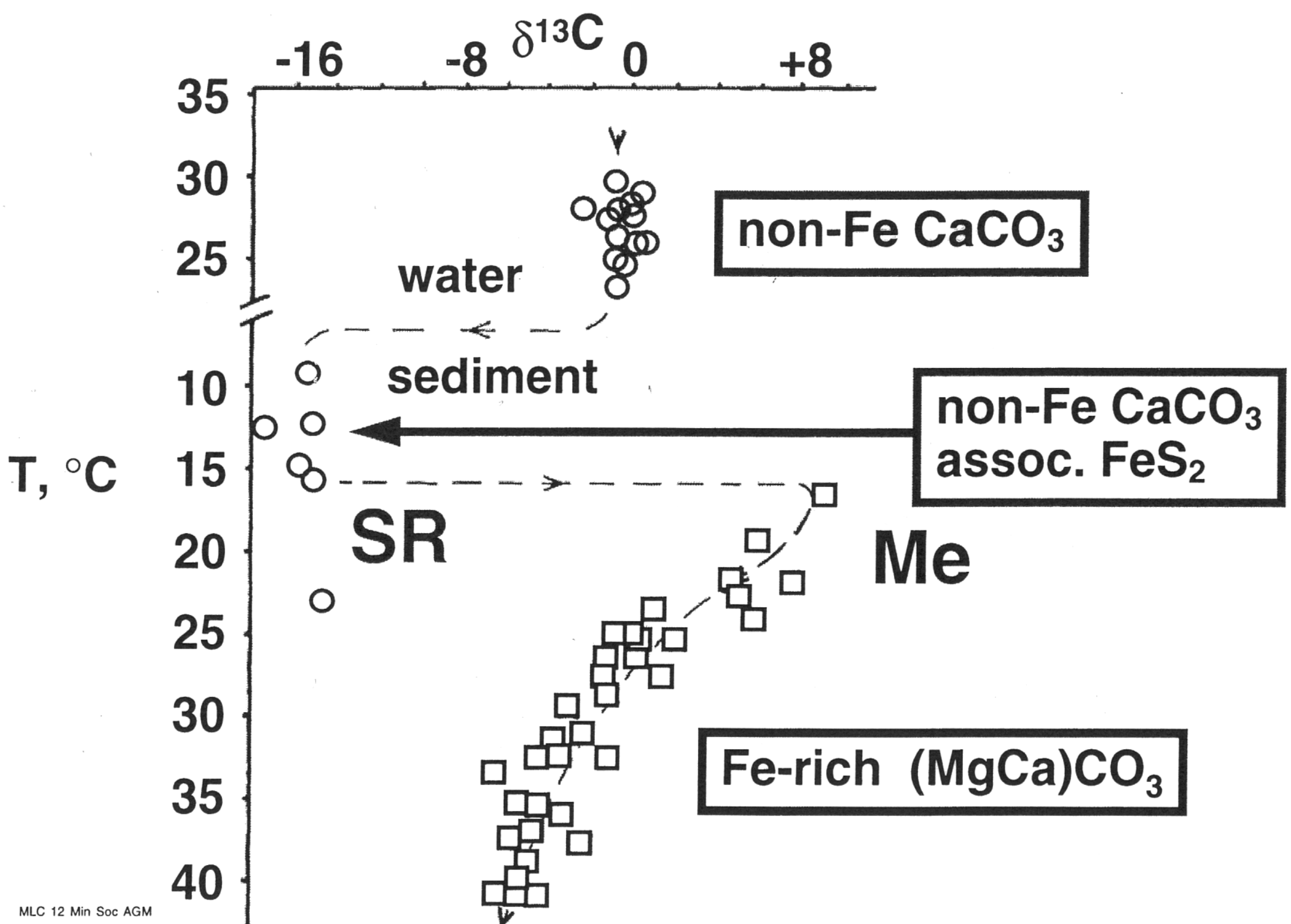
Canfield 1993

The energy yield of a biogeochemical process depends on the respective electron donor

Pathway and stoichiometry of reaction	ΔG^0 (kJ mol-1)
Oxic respiration:	
$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-479
Denitrification:	
$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	-453
Mn(IV) reduction:	
$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-$	-349
Fe(III) reduction:	
$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$	-114
Sulfate reduction:	
$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	-77
$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$	-152
$CH_3COO^- + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + HS^- + 2H_2O$	-41
Methane production:	
$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	-136
$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	-28
Acetogenesis:	
$4H_2 + 2CO_3^- + H^+ \rightarrow CH_3COO^- + 4H_2O$	-105
Fermentation:	
$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + 2H_2 + H^+$	10
$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + HCO_3^- + 3H_2 + H^+$	77

Jørgensen 2000

Carbon stable isotopes and the formation of diagenetic carbonate



Courtesy of Max Coleman

Early diagenesis in hypersaline settings

Stratifiaction in hypersaline water bodies or water bodies of variable salinity tends to favor the accumulation of organic matter in the sediment (preservation scenario) → abundant electron donors

Sulfate is the second most abundant anion in seawater. Marine depositional environments affected by evaporation tend to be rich in sulfate minerals → abundant electron acceptor

Formation of diagenetic carbonate and native sulfur

Concentrated sulfate in an evaporitic lagoon
during sedimentation or early diagenesis

syngenetic pathway

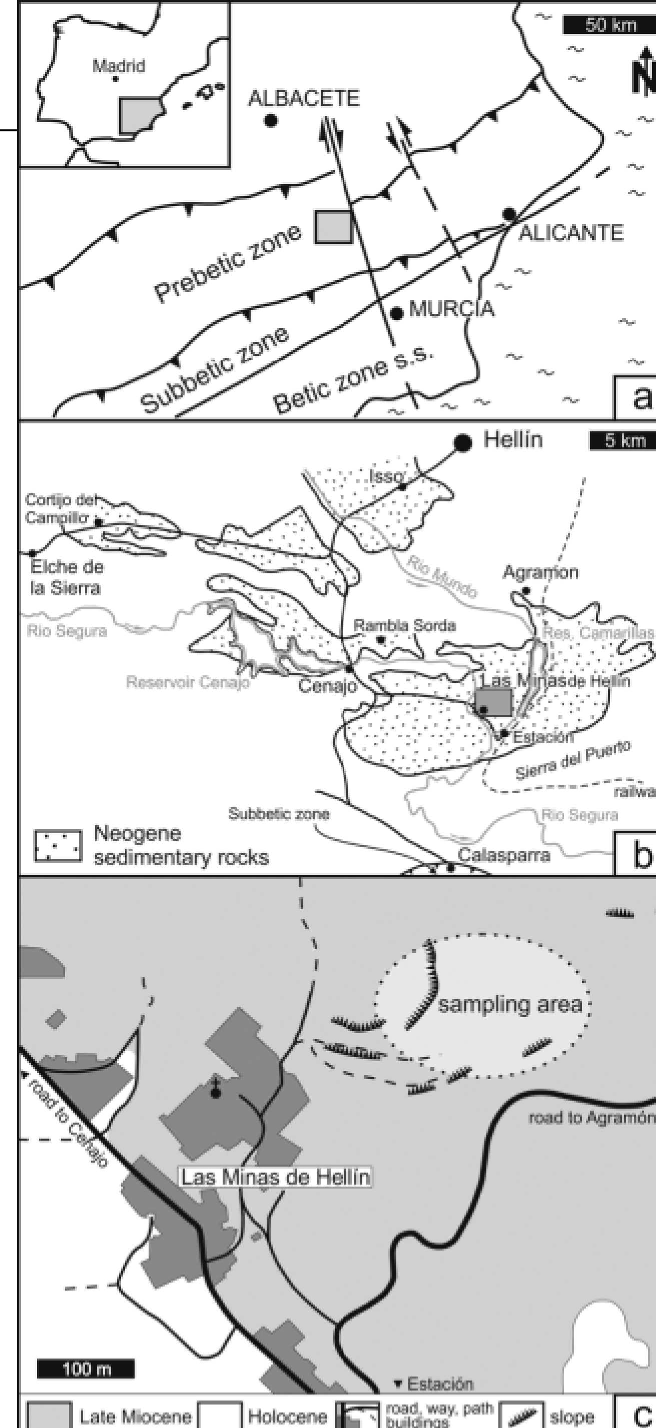
Sulfate from dissolution of gypsum or anhydrite
after burial and subsequent uplift

epigenetic pathway

Syngenetic sulfur formation

Case study: Hellín basin

Cenajo sub-basin

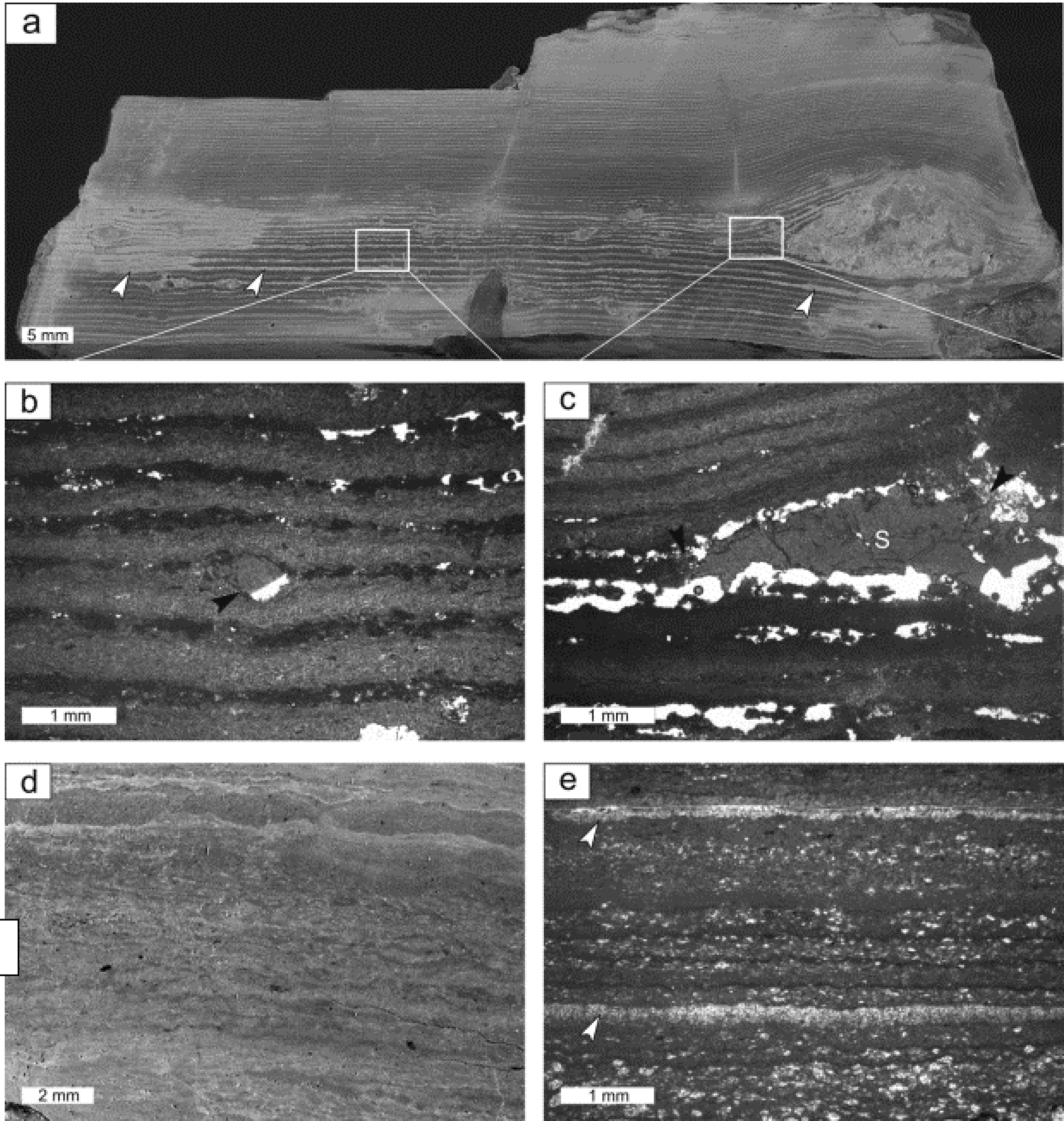


Native sulfur

sulfur enclosed in gypsum

sulfur enclosed in carbonate beds

Carbonate beds

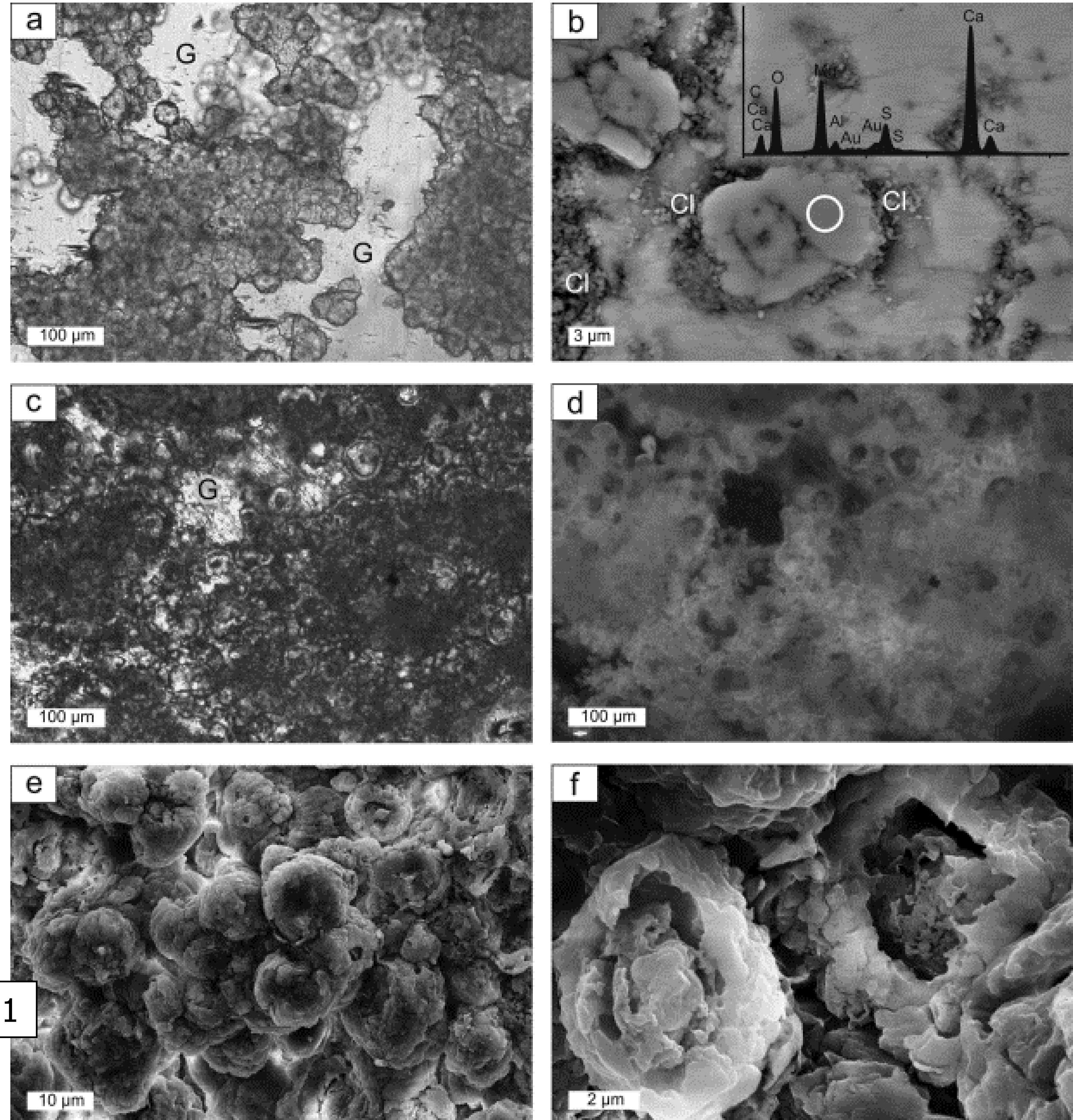


Lindtke et al. 2011

Spheroidal dolomite

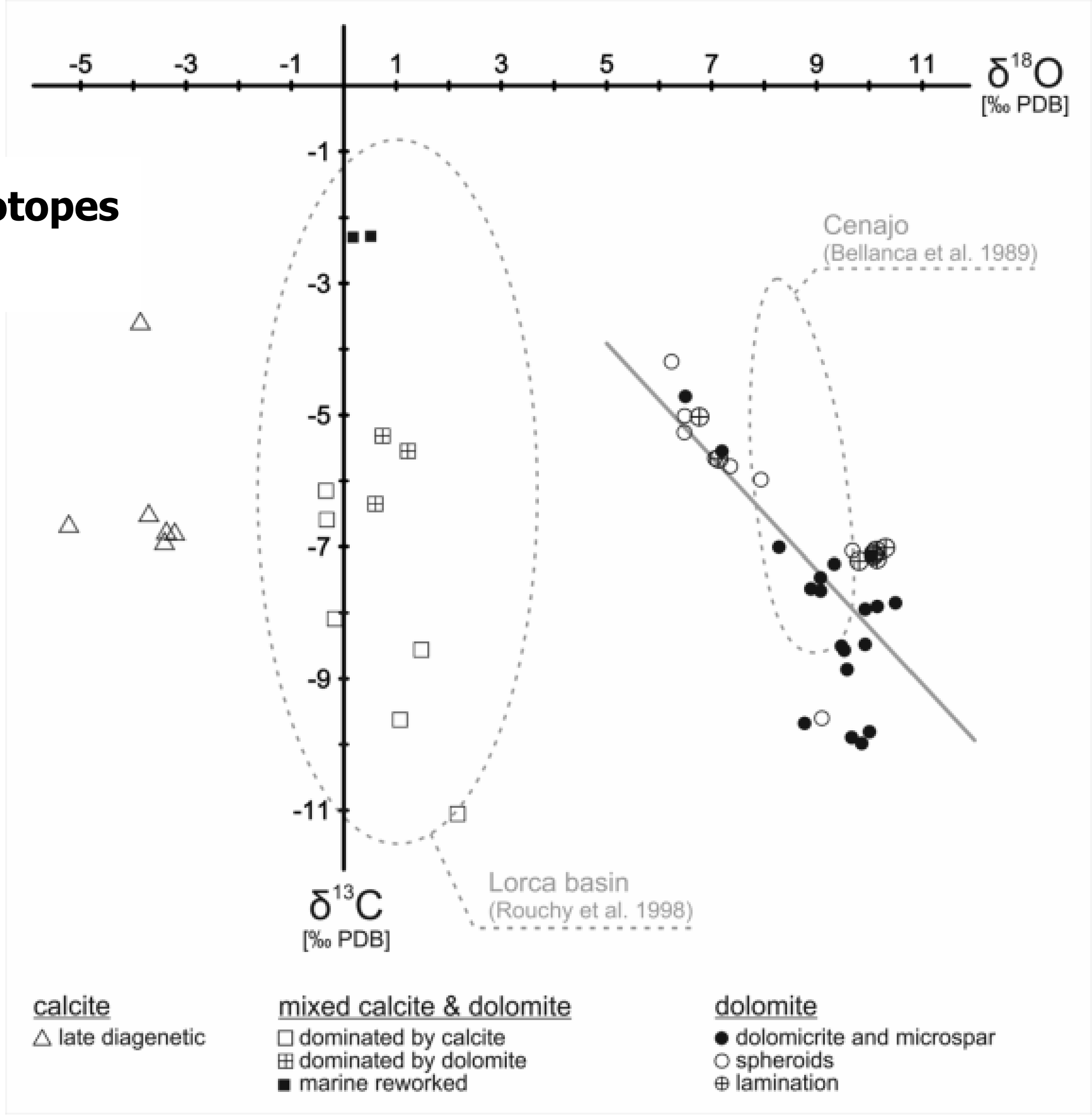
G = gypsum

Cl = clay minerals



Lindtke et al. 2011

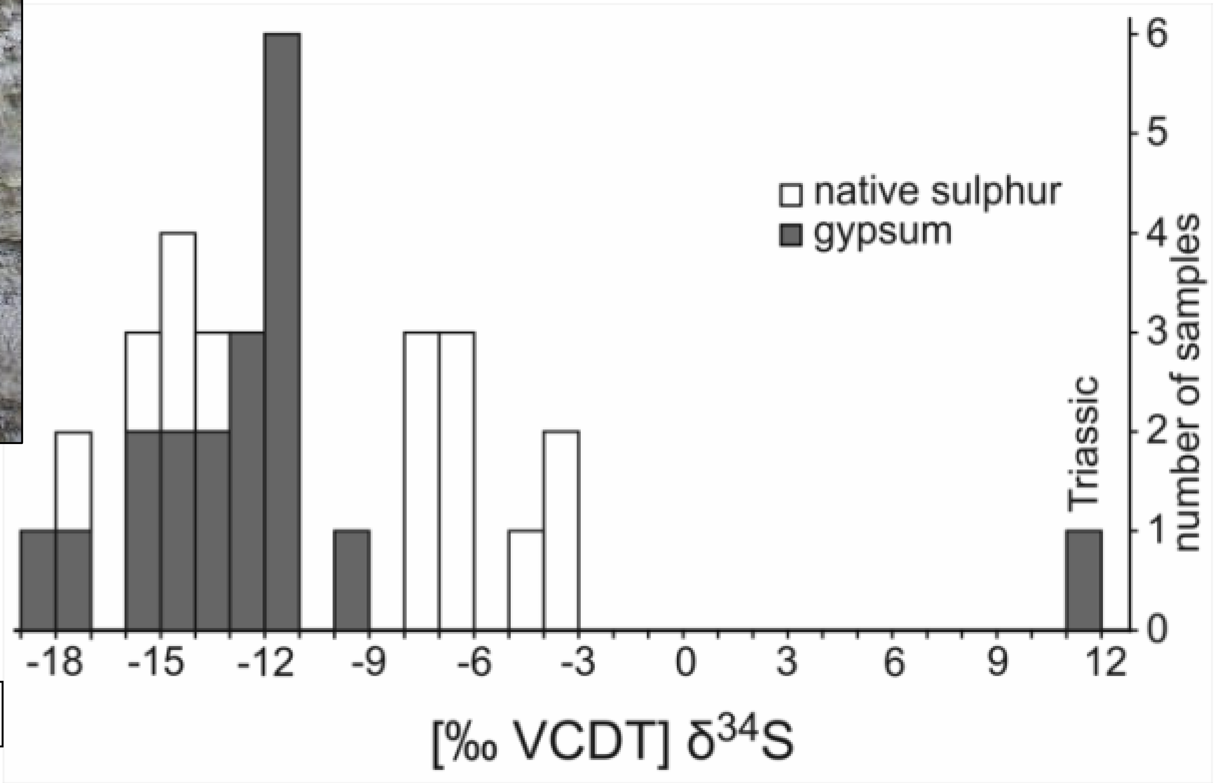
Stable carbon and oxygen isotopes of carbonate phases



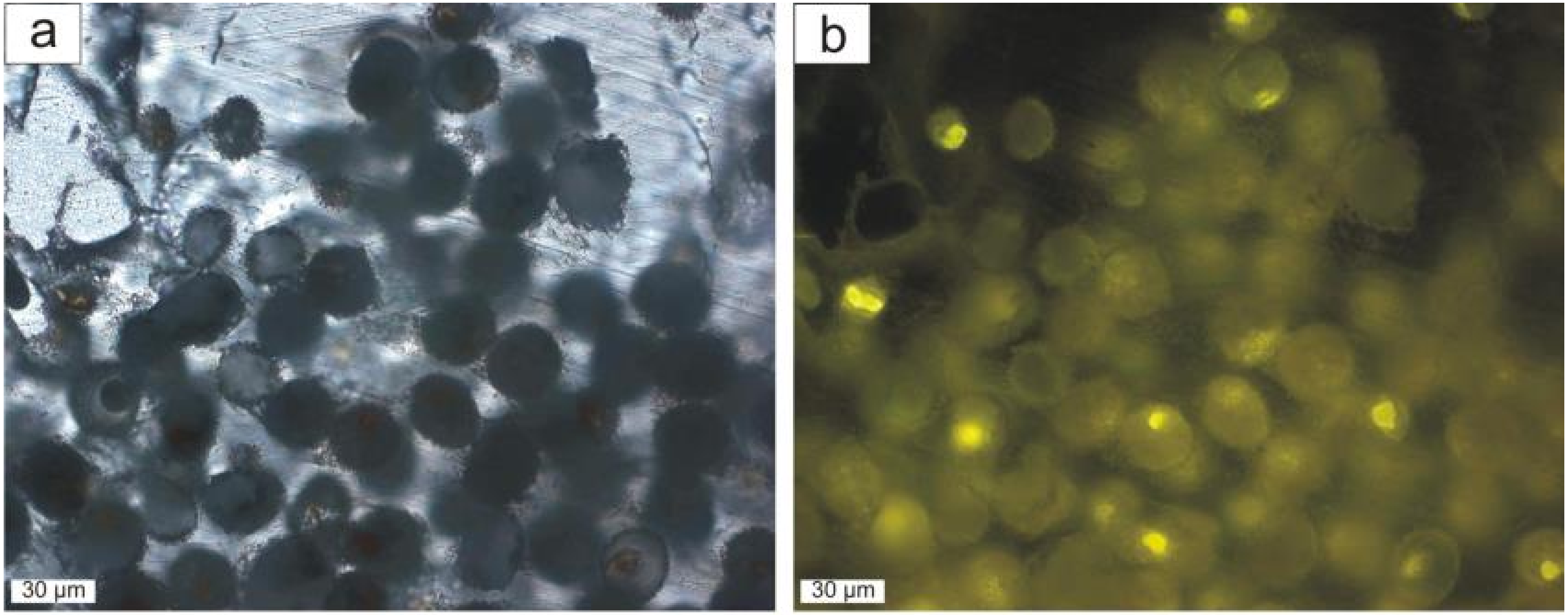
Lindtke et al. 2011

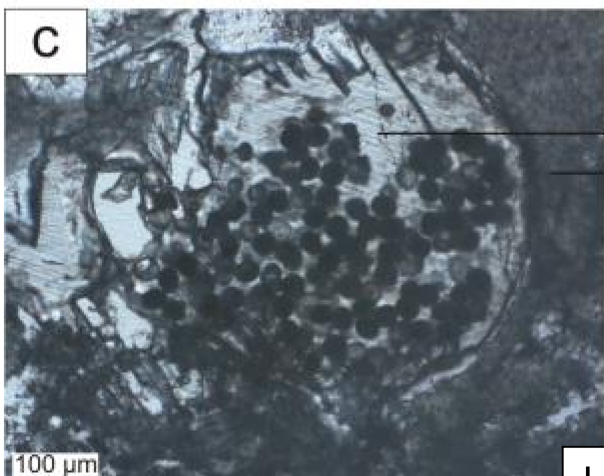
Stable sulfur isotopes

of native sulfur and gypsum phases



Lindtke et al. 2011





Fossilized sulfide-oxidizing bacteria

Lindtke et al. 2011

Formation of secondary carbonate and native sulfur

Dissolution of gypsum

(1) $CaSO_4 \times 2\ H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2\ H_2O$

Bacterial sulfate reduction

(2) $SO_4^{2-} + 2\ CH_2O$ (org. mat.) $\rightarrow 2\ HCO_3^{-} + H_2S$

Carbonate precipitation

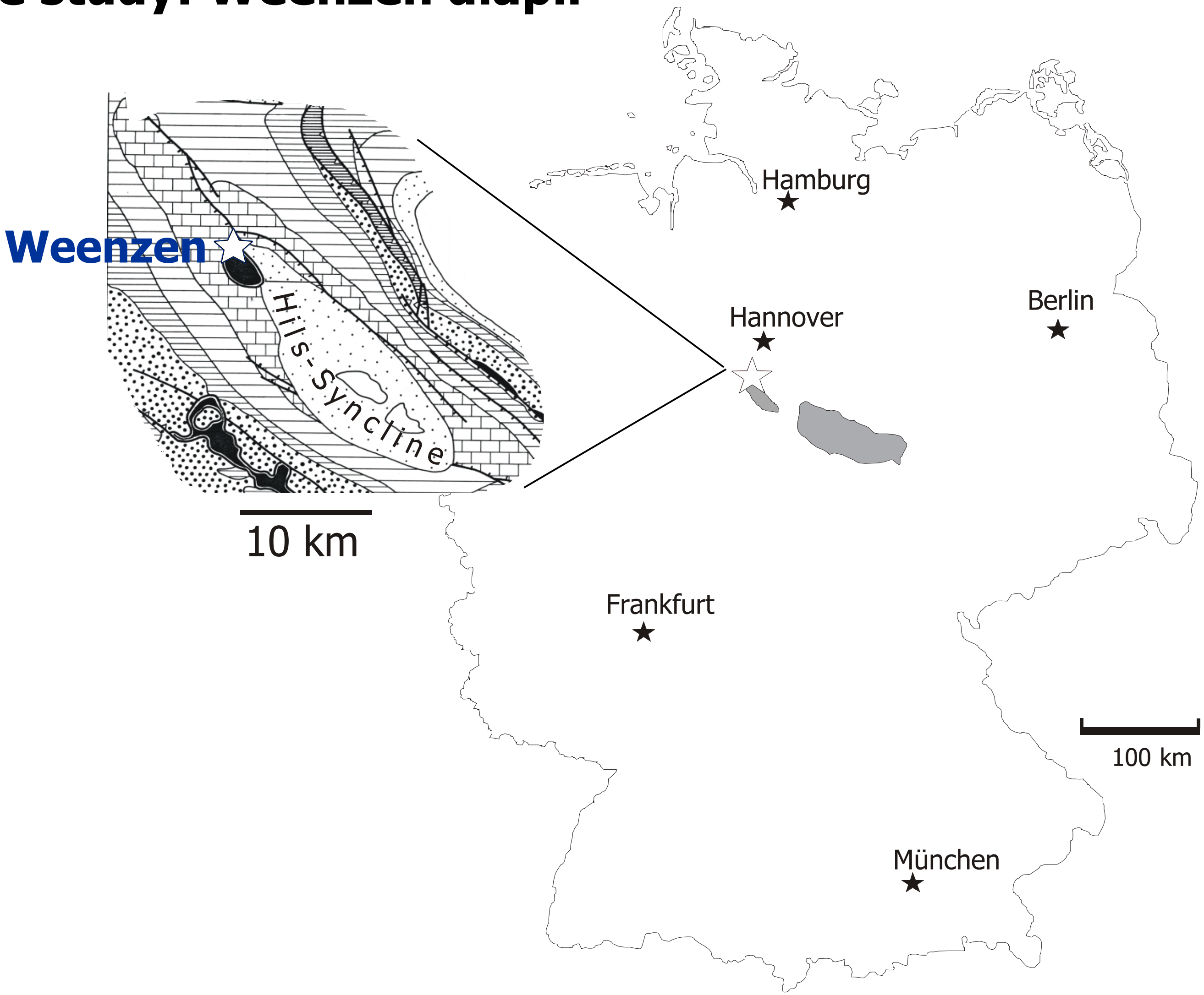
(3) $Ca^{2+} + 2\ HCO_3^{-} \rightarrow CaCO_3 + H_2O + CO_2$

Sulfur formation

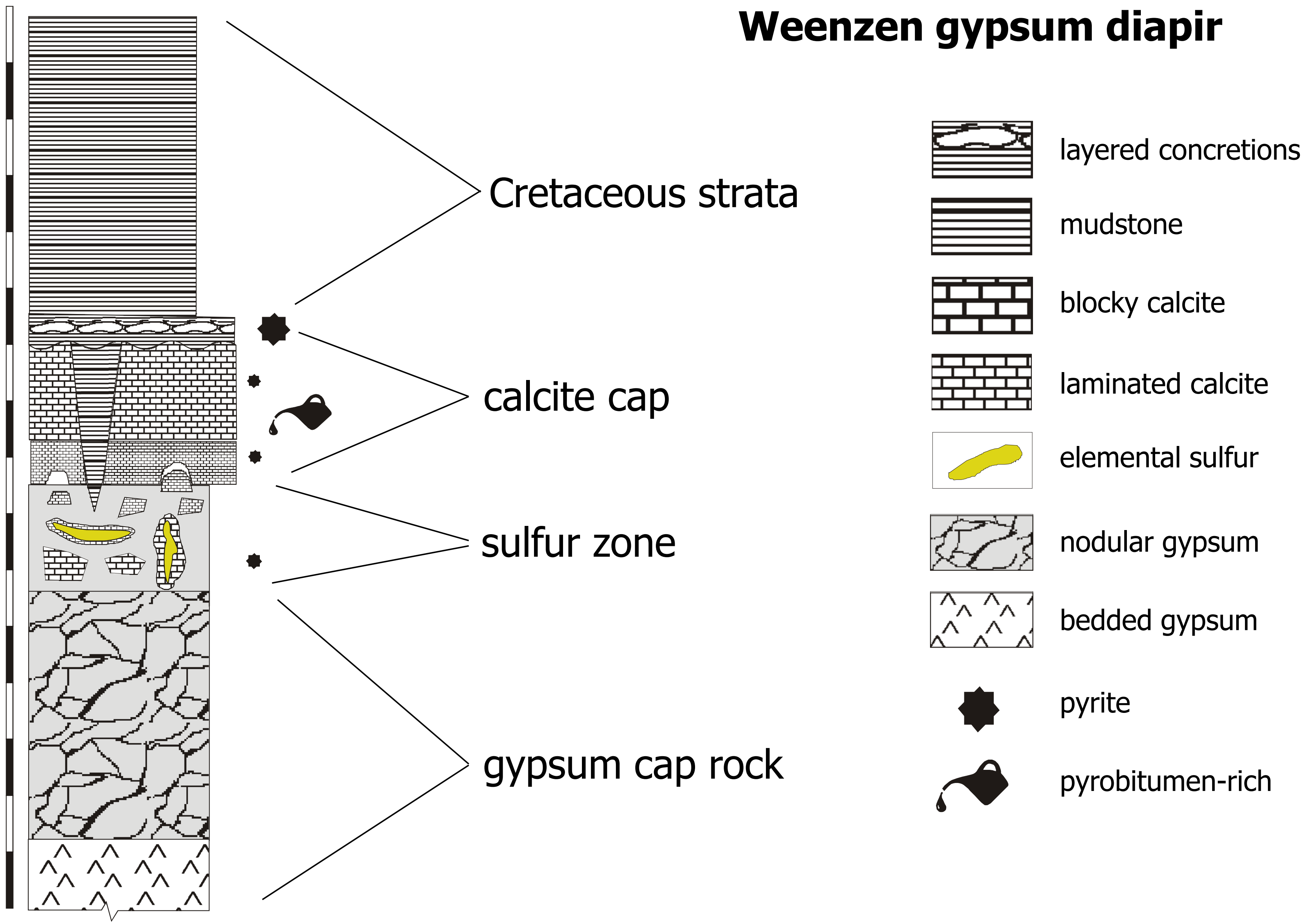
(4) $2\ H_2S + O_2 \rightarrow 2\ S^0 + 2\ H_2O$

Epigenetic sulfur formation

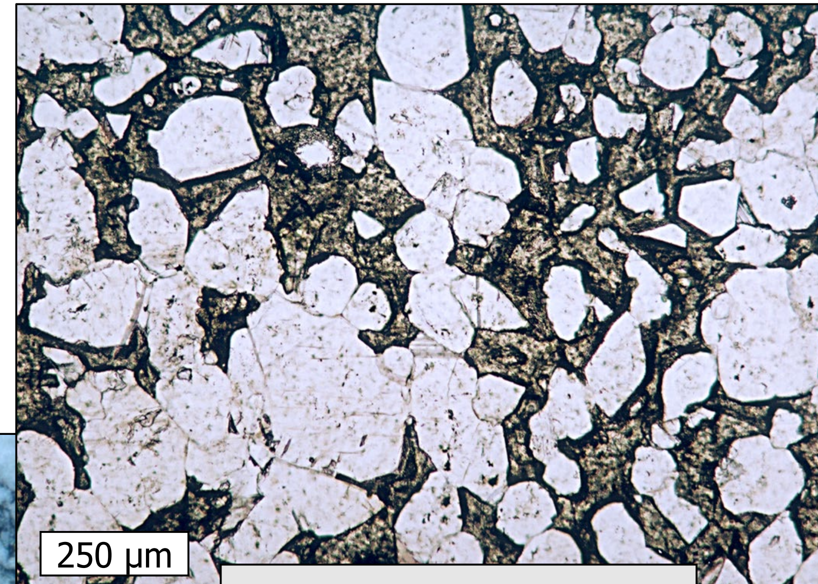
Case study: Weenzen diapir



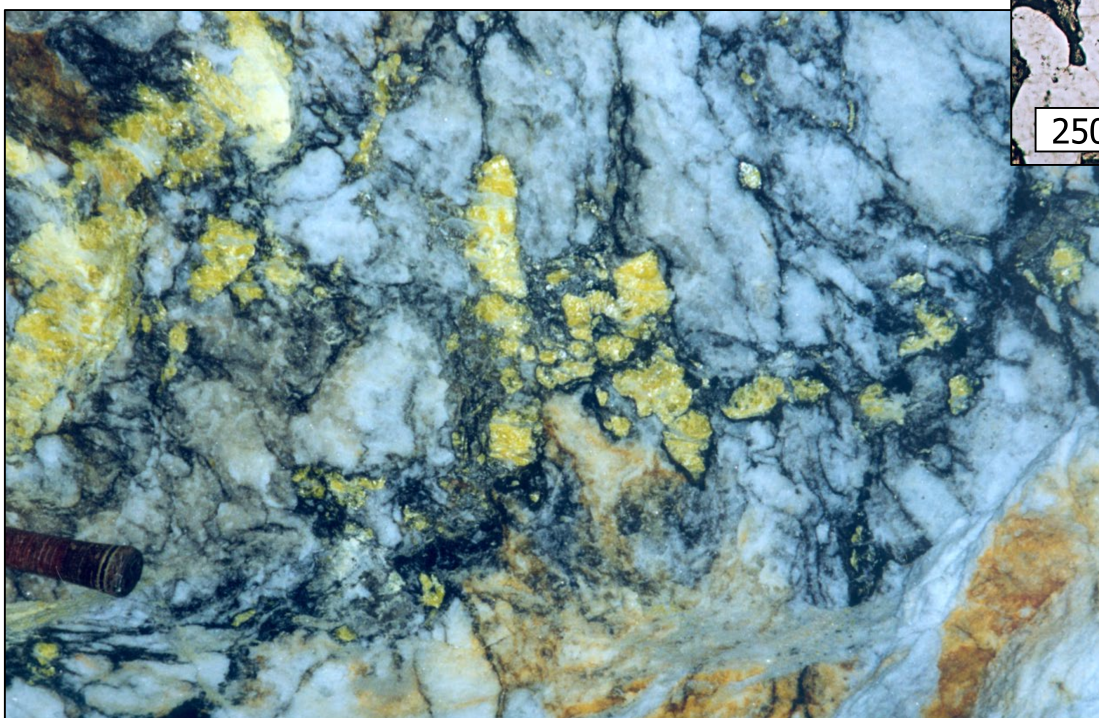
Weenzen gypsum diapir

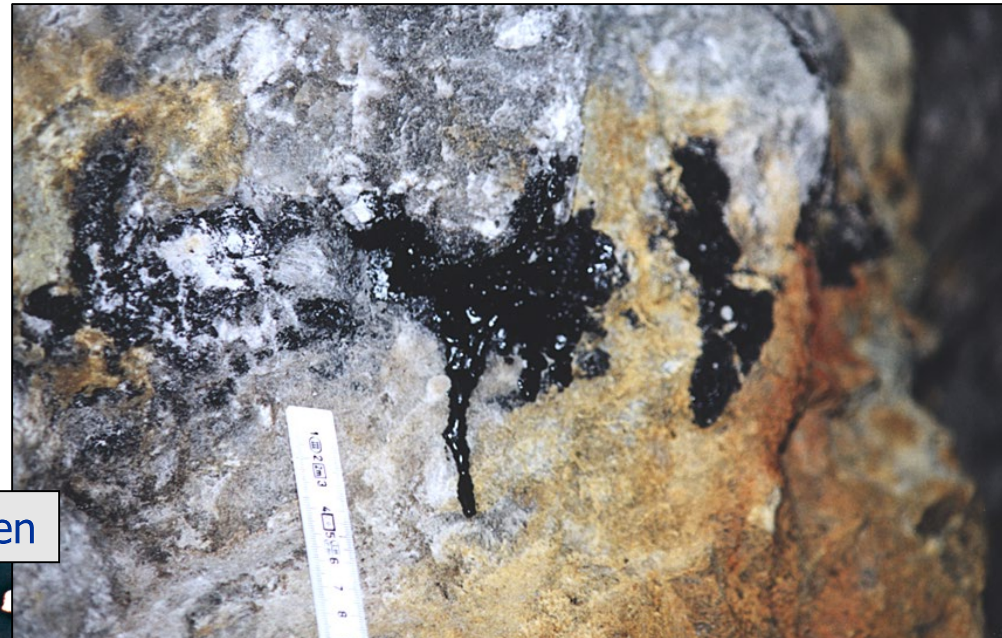


Weenzen gypsum diapir

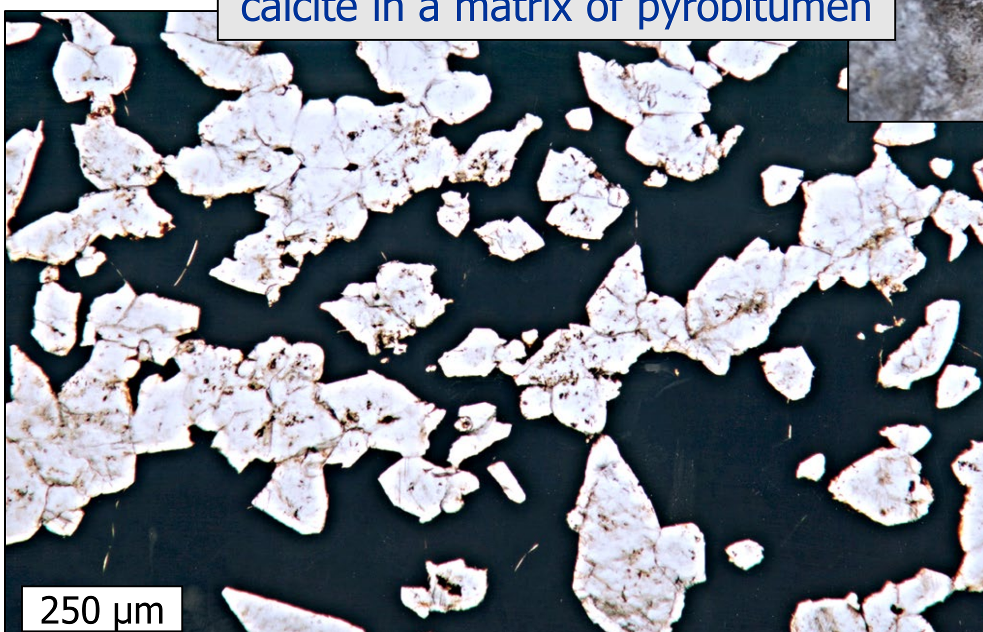


elemental sulfur and subhedral calcite

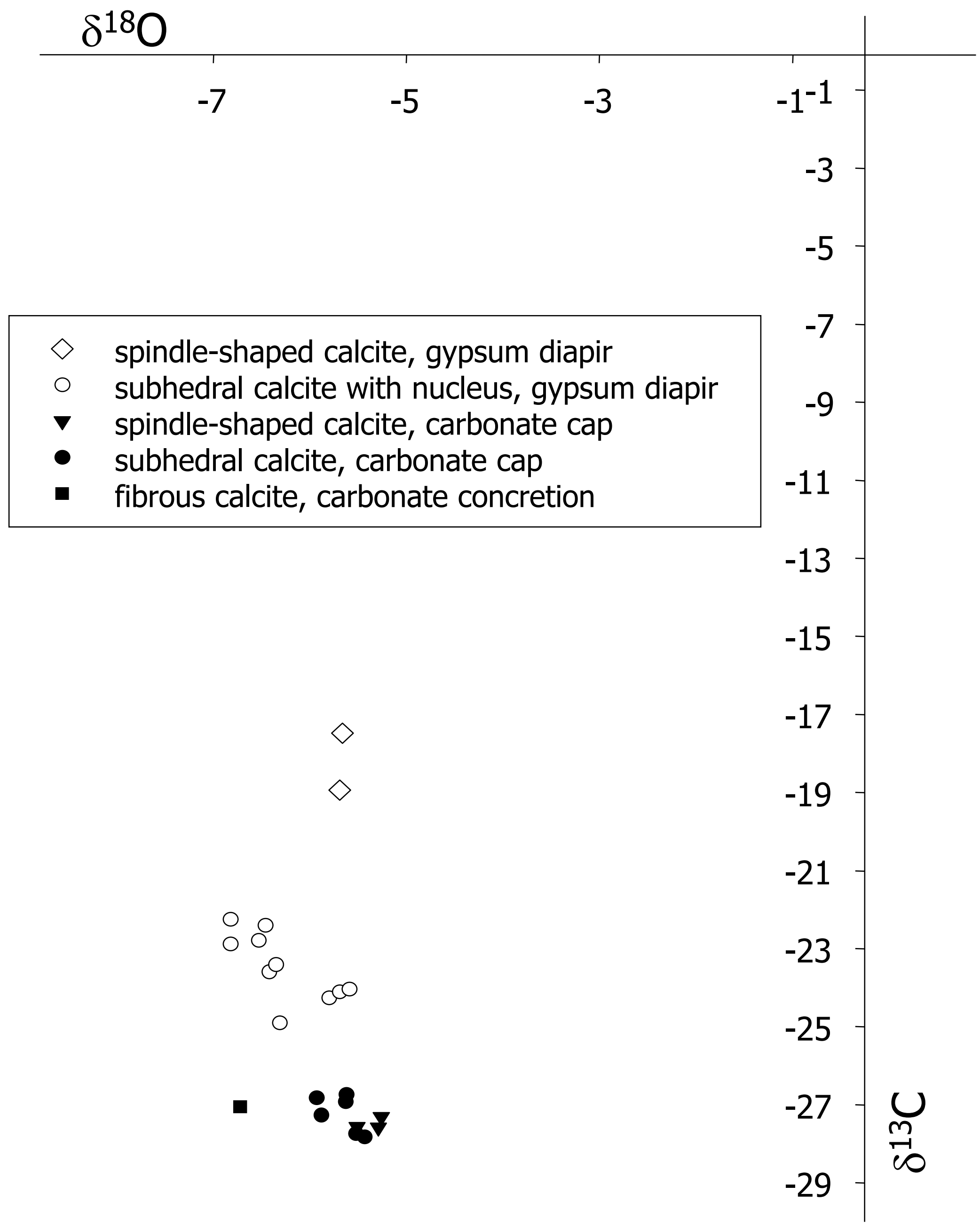




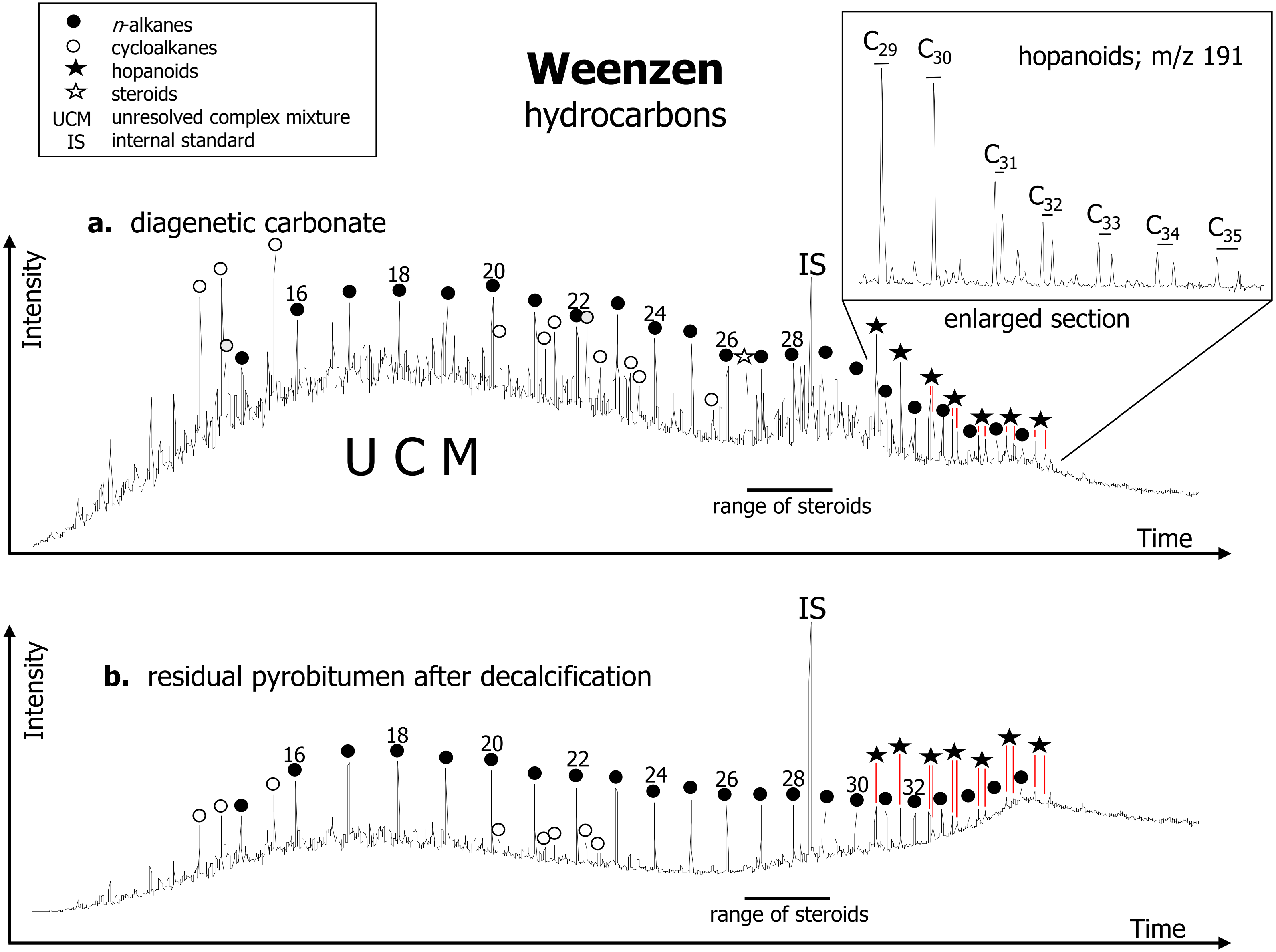
calcite in a matrix of pyrobitumen



C and O stable isotopes
Weenzen



Weenzen
hydrocarbons



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Carbonate precipitation

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~~Sulfur formation~~

~~(4) $2\,H_2S + O_2 \rightarrow 2\,S^0 + 2\,H_2O$~~

The issue with sulfide oxidation in the subsurface

frontiers in Microbiology
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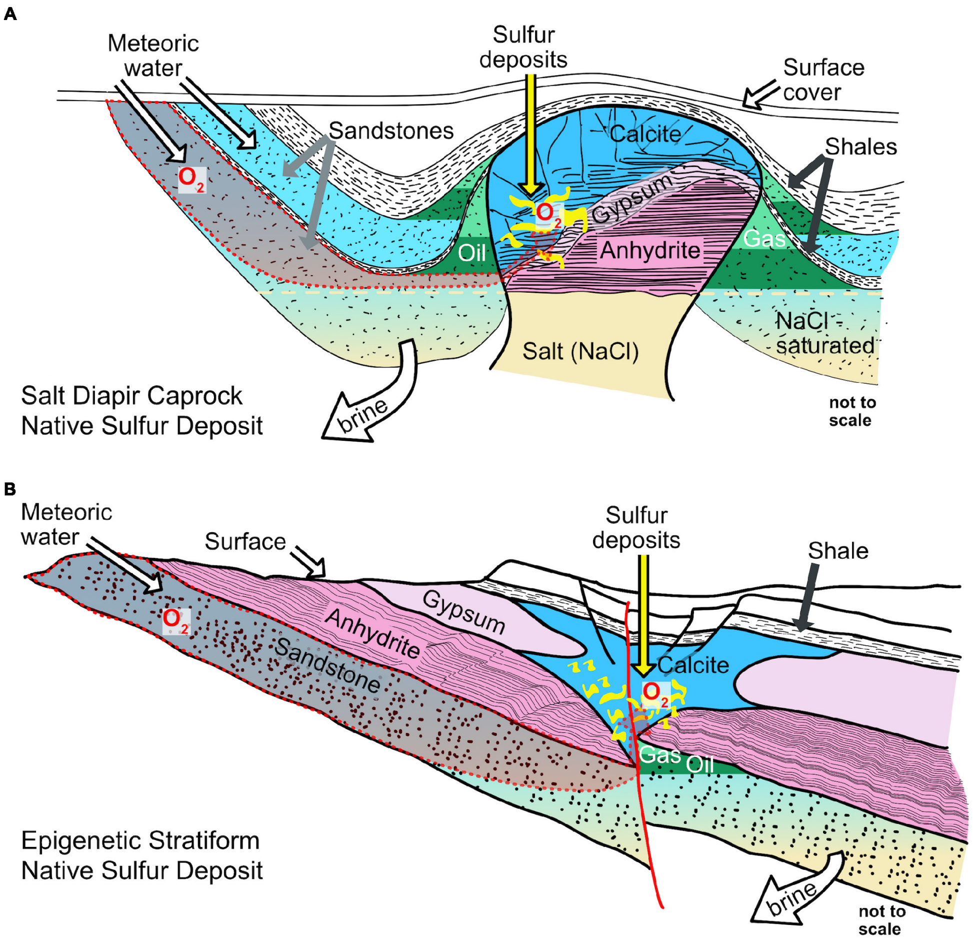
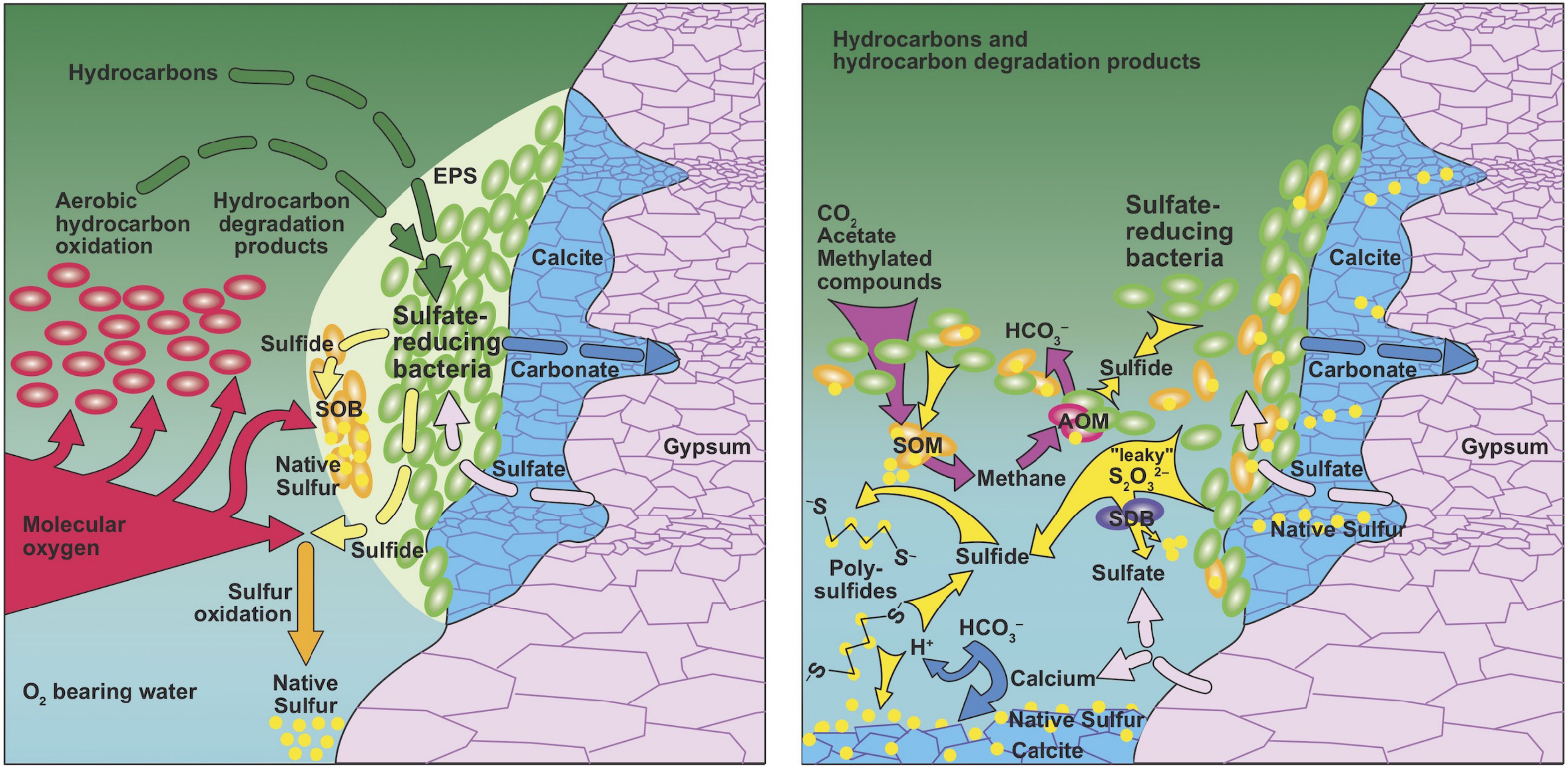


Formation of Large Native Sulfur Deposits Does Not Require Molecular Oxygen

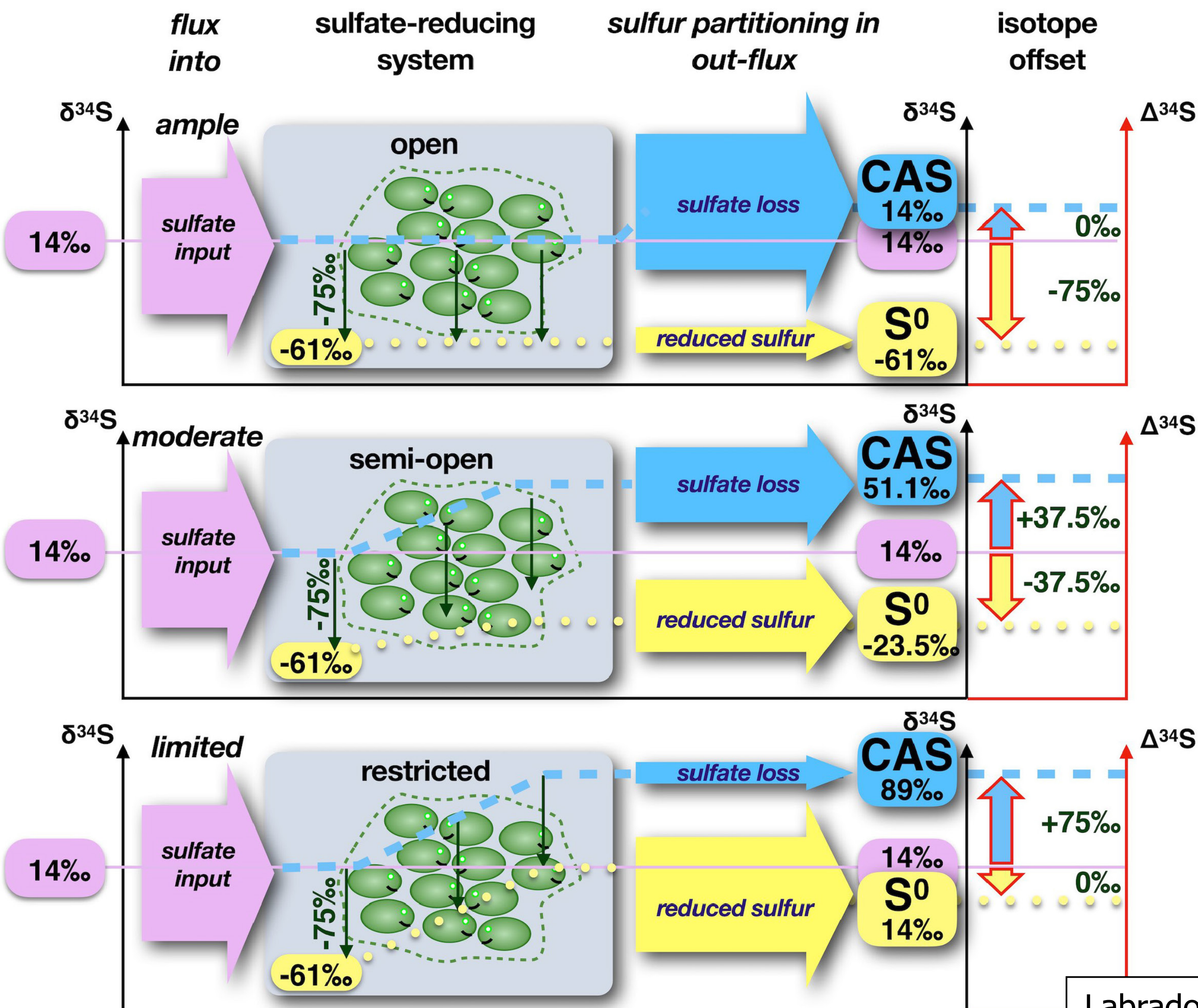
Amanda L. Labrado[1]*, Benjamin Brunner[1], Stefano M. Bernasconi[2] and Jörn Peckmann[3]

Formation of native sulfur with and without molecular oxygen



Labrado et al. 2019

SOB = sulfide-oxidizing bacteria; SDB = sulfur disproportionating bacteria



Labrado et al. 2019

A selection of candidate mechanisms

(1) sulfate reduction process producing sulfur of intermediate oxidation state

(2) coupling of sulfide oxidation to methanogenesis utilizing methylated compounds, acetate, or carbon dioxide

$$4H_2S + HCO_3^- + H^+ \rightarrow CH_4 + 4S^0 + 3H_2O$$

$$CH_3COOH^- + H^+ + 4H_2S \rightarrow 2CH_4 + 4S^0 + 2H_2O$$

$2H_2S + CH_3OH \rightarrow 4CH_4 + 4S^0$ – dimethyl sulfide based methanogenesis

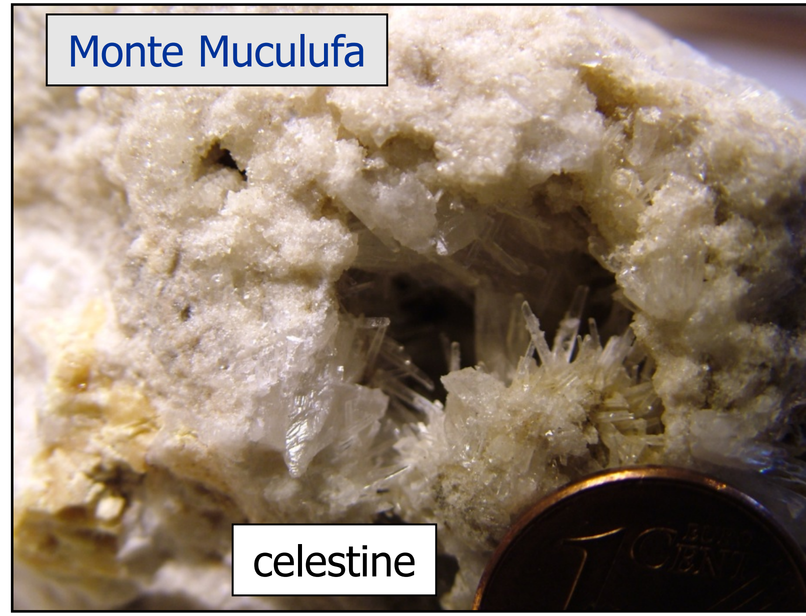
(3) ammonium oxidation coupled to sulfate reduction

$$2NH_4^+ + SO_4^{2-} \rightarrow N_2 + S^0 + 4H_2O$$

(4) sulfur comproportionation of sulfate and sulfide

$$3H_2S + CaSO_4 \text{ x } 2H_2O + CO_2 \rightarrow 4S^0 + CaCO_3 + 5H_2O$$

Calcare solfifero

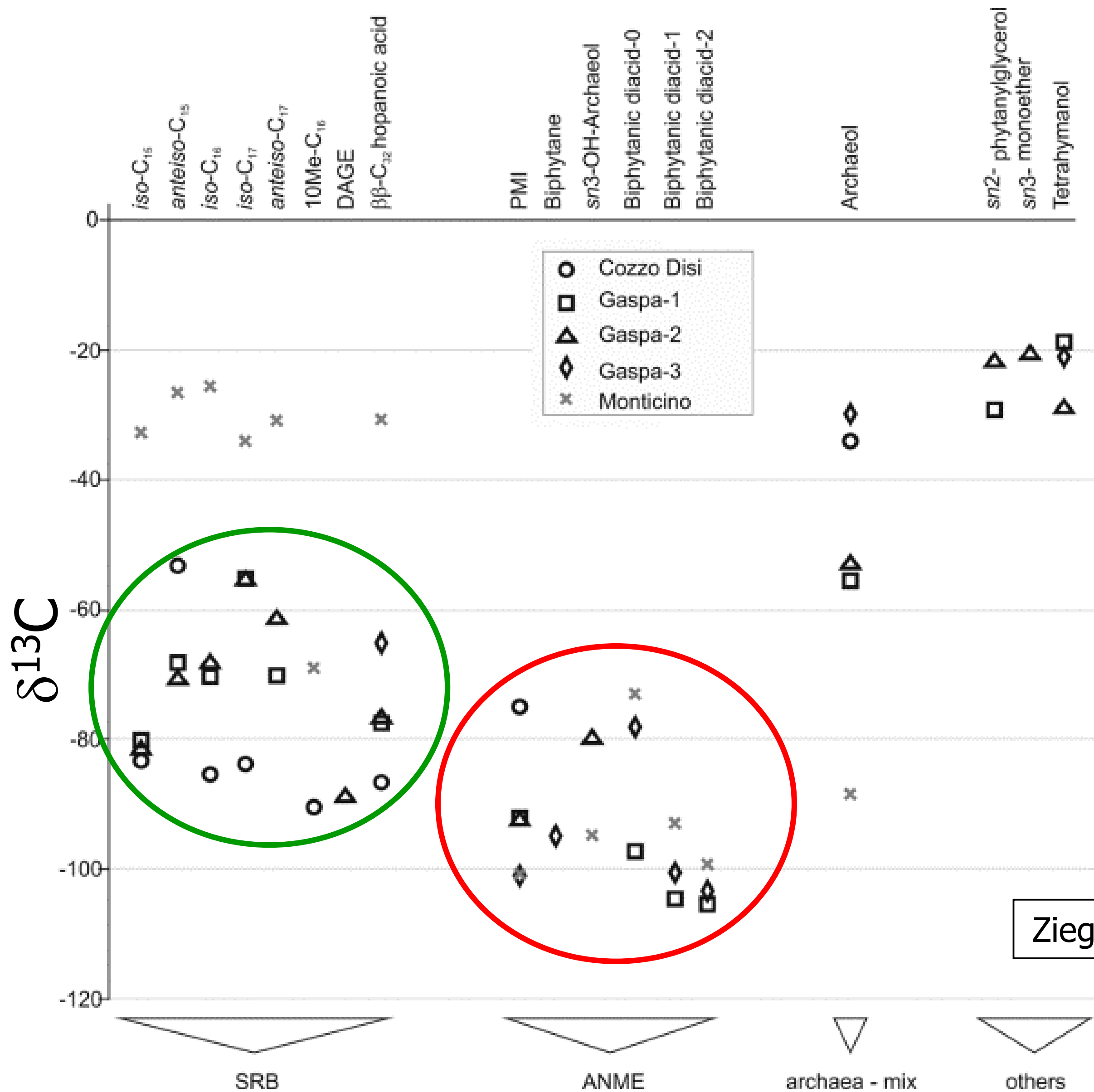


Calcare solfifero

Ziegenbalg et al. 2010

Location Lat.; Long.	$\delta^{13}C_{carbonate}$	$\delta^{18}O_{carbonate}$	Salinity indicators
Cozzo Disi **37°30’51‘‘N; 13°40’45‘‘E**	–49 to –29‰	+4 to +9‰	Calcite pseudomorphs after lenticular gypsum; enrichment in ^{18}O
Gaspa **37°37‘00‘‘N; 14°12’26‘‘E**	–46 to –34‰	+3 to +8‰	Calcite pseudomorphs after lenticular gypsum; enrichment in ^{18}O
Monticino **44°13’29‘‘N; 11°45’50‘‘E**	–27 to –23‰	+7‰	Enrichment in ^{18}O

Ziegenbalg et al. 2012



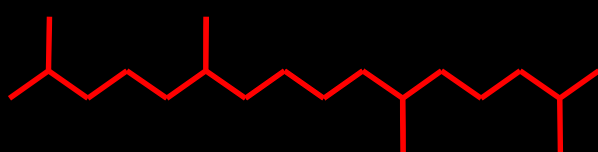
green: SRB
red: ANME = methanotrophic archaea

Ziegenbalg et al. 2012

Anaerobic oxidation of methane – AOM

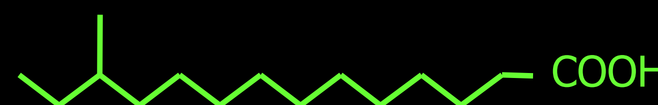
Boetius et al. 2000

methanotrophic archaea



crocetane

sulfate-reducing bacteria

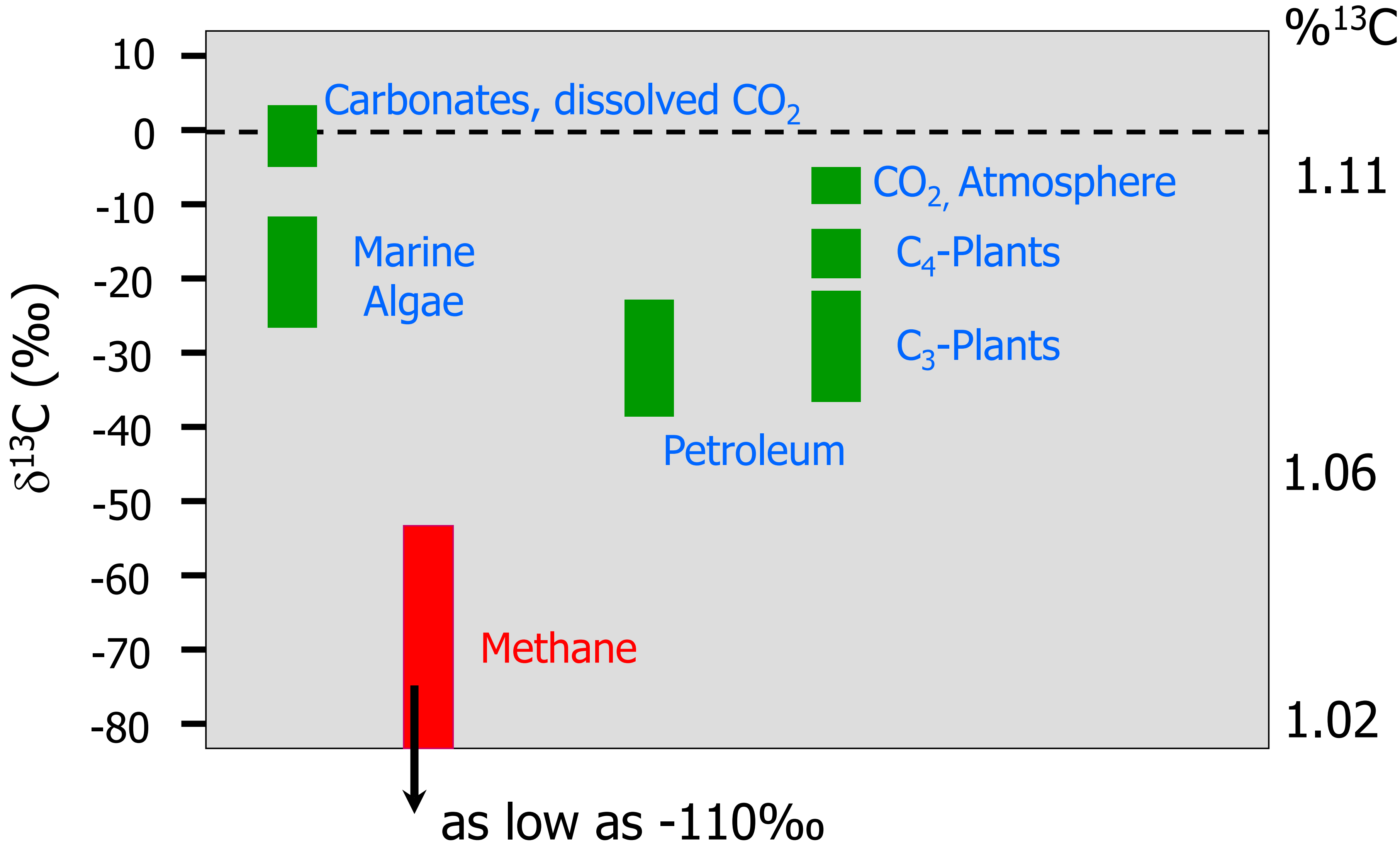


ai-C_{15} fatty acid

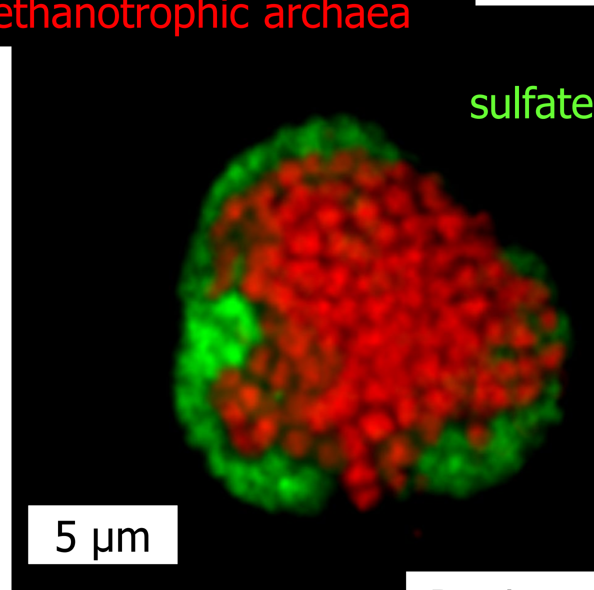
Peckmann and Thiel 2004

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

Isotopic compositions of different carbon pools

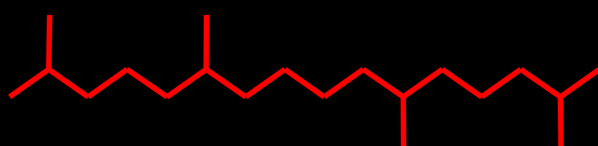


Anaerobic oxidation of methane – AOM



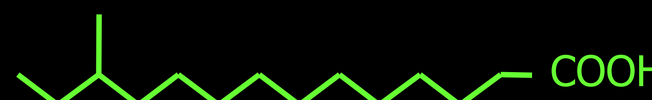
Boetius et al. 2000

methanotrophic archaea



crocetane

sulfate-reducing bacteria

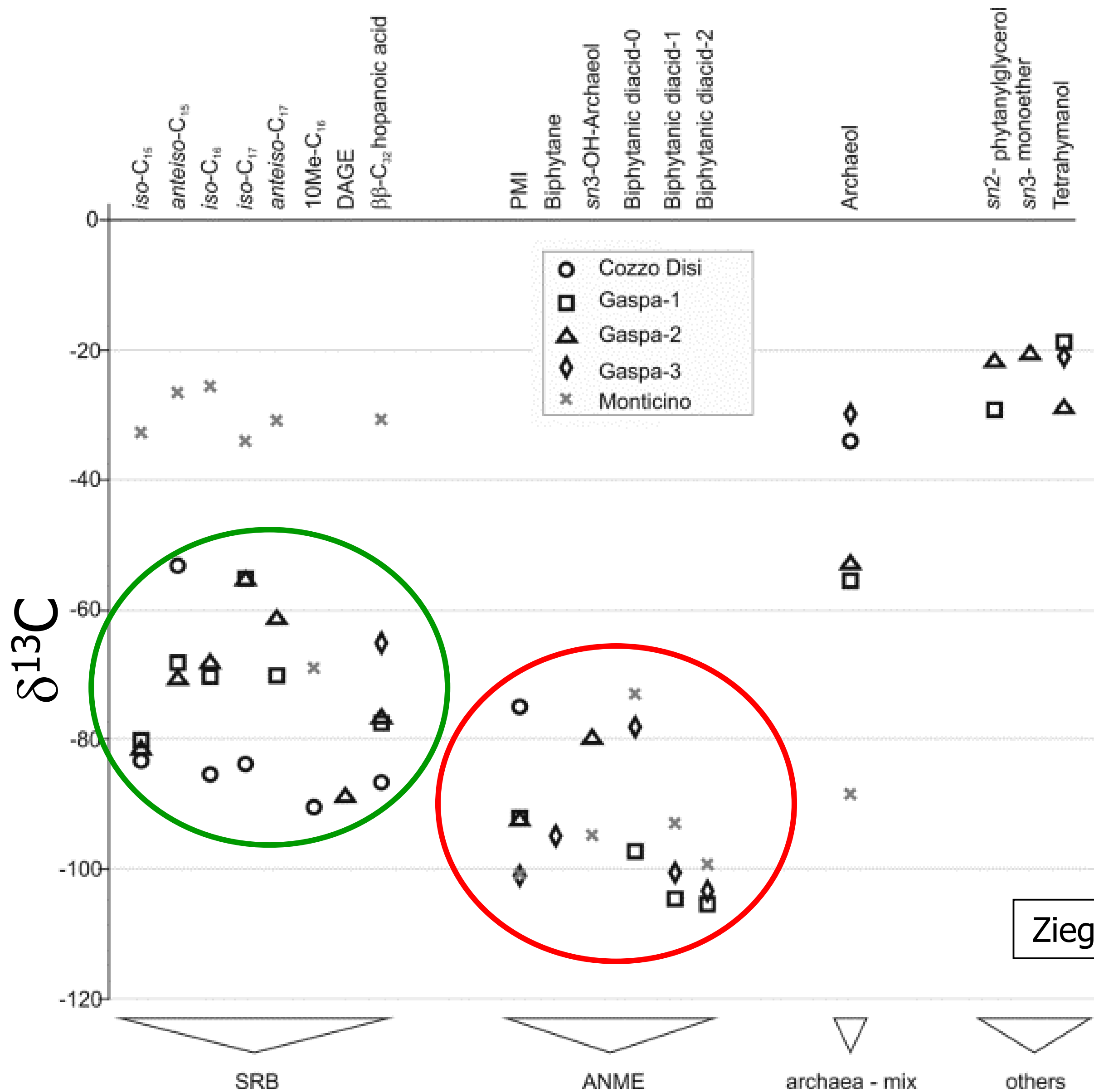


ai-C_{15} fatty acid

Peckmann and Thiel 2004

$CH_4 + SO_4^{2-} \rightarrow HCO_3^{-} + HS^{-} + H_2O$ results in

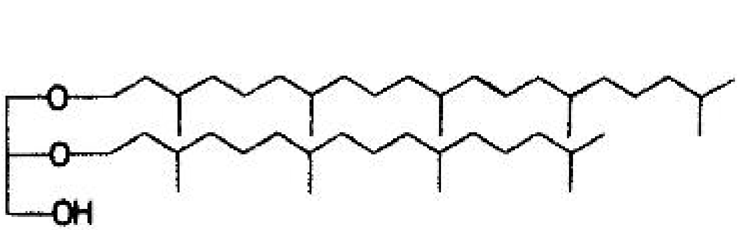
low $\delta^{13}C_{carbonate}$ and low $\delta^{13}C_{biomass\ incl.\ lipids}$ values



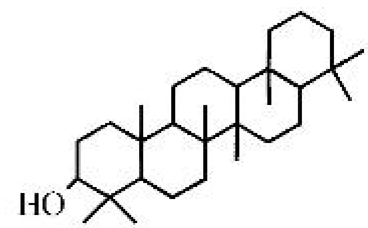
green: SRB
red: ANME = methanotrophic archaea

Ziegenbalg et al. 2012

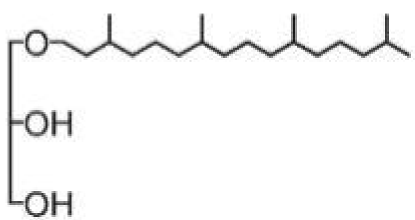
Hypersaline conditions revealed by molecular fossils



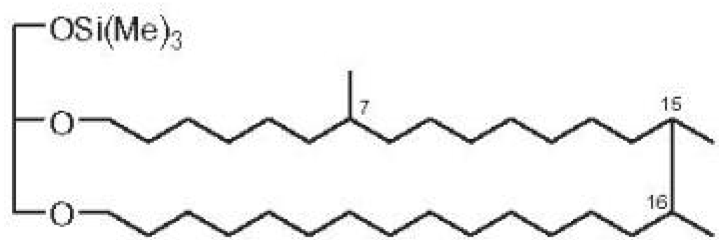
extended archaeol



tetrahymanol



phytanyl monoether



non-isoprenoidal macrocyclic glycerol diether

Take home notes

1. Early diagenesis is driven to a large extent by biogeochemical reactions

2. Hypersaline settings favor the accumation of organic matter, resulting in intense diagenesis

3. Formation of native sulfur in epigenetic settings does not require molecular oxygen

4. AOM occurs in hypersaline environments as well

5. Calcare solfifero resulted from metabolism driven precipitation

Messinian geomicrobiology team – past and presence

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Simone Ziegenbalg

The Messinian Endeavor

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