Archaeal Biomarker Records in Marine Sediments Impacted by Methane Transport: Insights from Peru Margin

Sajjad Akam[1], Hussain Abdulla[2], Yige Zhang[3], Joshua Avalos[2], and Richard Coffin[2]

[1]Iowa State University
[2]Texas A&M University Corpus Christi
[3]Texas A&M University

November 24, 2022

Abstract

The transport of methane from deep sediments towards the seafloor is widespread in ocean margins and has important biogeochemical implications for the deep ocean [1]. A significant portion (>80%) of methane entering the shallow sediments from below at present is oxidized by microbially-driven anaerobic oxidation of methane (AOM), which mainly involves a microbial consortium of anaerobic methanotrophic archaea (ANME) and sulfate-reducing bacteria. Isoprenoid Glycerol dialkyl glycerol tetraethers (GDGTs) derived from core lipid membranes of ANMEs are often well preserved in sediment records. Methane Index (MI) is an organic geochemical proxy for methane seepage intensity which weighs in the relative proportion of GDGTs (GDGT-1,-2, and -3) preferentially synthesized by ANMEs with that of non-methane-related biomarker contribution from planktonic and benthic sources (Crenarchaeols) [2]. This study analyzed the GDGT composition of sedimentary core lipids from IODP Site 1230 (Peru Margin) using two silica columns and a high-resolution and accurate mass Orbitrap Fusion Mass Spectrometer. Our results report novel GDGT isomers with concentration peaking at the Sulfate-Methane Transition Zones (SMTZ) with the highest AOM activity around 8 mbsf. Further, these isomers were almost absent above and below the SMTZ. Our observations suggest that these characteristic isomers of GDGT compounds preserved at the SMTZ depth are sourced from ANMEs. Identification of these novel isomers has important implications in refining the MI and additional GDGT based palaeoceanographic proxies like TEX86. 1. Akam et al. (2020), Frontiers in Marine Science 7, 206. 2. Y. G. Zhang et al. (2011), Earth and Planetary Science Letters 307, 525-534.

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1 Geological and Atmospheric Science, Iowa State University, (*correspondence: sajjad@iastate.edu)
2 Physical & Environmental Science, Texas A&M University-Corpus Christi
3 Department Of Oceanography, Texas A&M University

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This study analyzed the GDGT composition of sedimentary core lipids from IODP Site 1230 (Peru Margin) using two silica columns and a high-resolution and accurate mass Orbitrap Fusion Mass Spectrometer. Our results report novel GDGT isomers with concentration peaking at the Sulfate-Methane Transition Zones (SMTZ) with highest AOM activity around 8 mbsf. Further, these isomers were almost absent above and below the SMTZ. Our observations suggest that these characteristic isomers of GDGT compounds preserved at the SMTZ depth are sourced from ANMEs. Identification of these novel isomers has important implications in refining the MI and additional GDGT based palaeoceanographic proxies like TEX86.

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IODP INTERNATIONAL OCEAN DISCOVERY PROGRAM

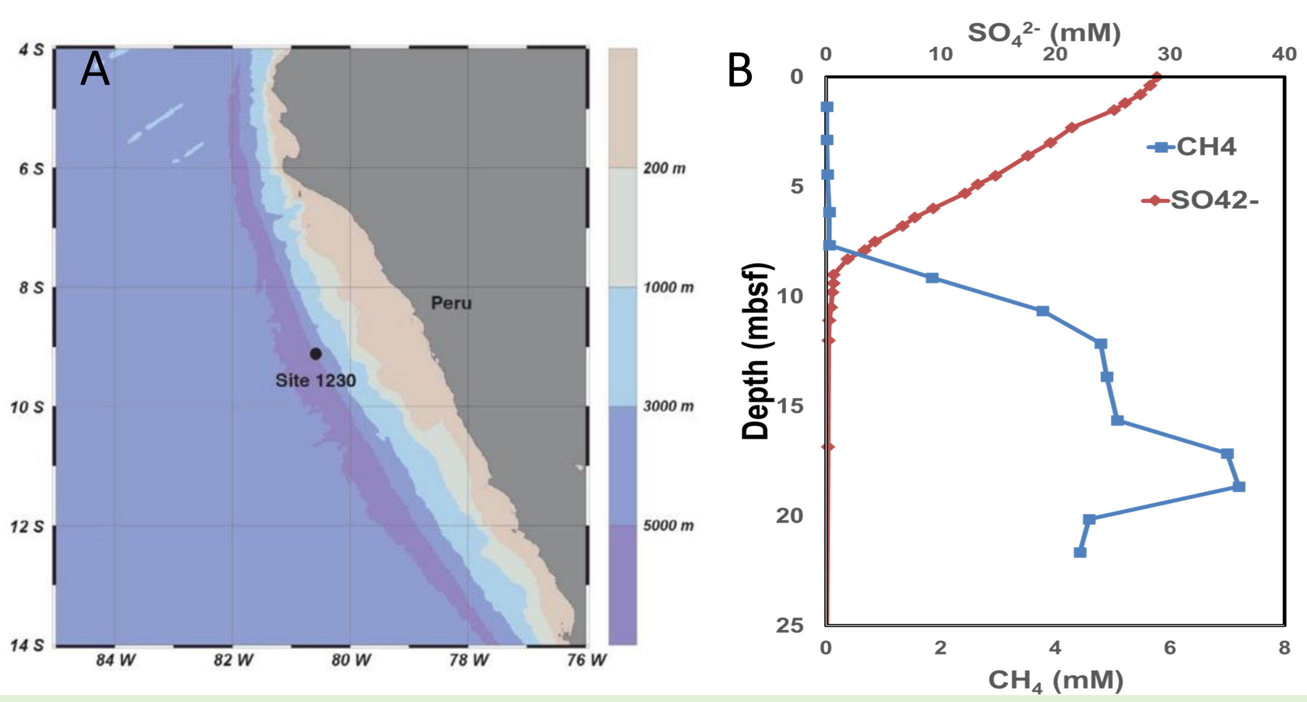
Abstract

- We analyzed isoprenoid glycerol dialkyl glycerol tetraethers (GDGTs), core lipid membranes produced primarily by archaea, preserved in a sediment core from Peru margin (ODP Site 1230).
- The study site was characterized by upward methane flux from deep sediment towards the seafloor and consequential anaerobic methane oxidation (AOM) involving anaerobic methanotrophic archaea (ANME)
- GDGT analysis was performed via high-resolution UPLC approach using two silica columns and Orbitrap Fusion Mass Spectrometer. This approach enabled efficient separation of GDGT isomers
- We observed potentially novel GDGT isomers for GDGT-1, -2, and -3 with concentrations peaking at sediment depths coinciding with the sulfate-methane transition zones and highest AOM activity, suggesting that these isomers are sourced by ANMEs
- Results suggest prospective refinement of GDGT-based paleo proxies like Methane Index (MI) and TEX86

Introduction

Transport of methane from deep sediments towards the seafloor is widespread in ocean margins and has important biogeochemical implications for the deep ocean. A significant portion (>80%) of methane entering the shallow sediments from below at present are oxidized by microbially-driven AOM, which mainly involves a microbial consortium of ANME and sulfate-reducing bacteria. Sulfate-methane transition zone (SMTZ) is the depth at which this sulfate-driven AOM predominantly occurs (Fig. 1). Methane Index (MI) is an organic geochemical proxy (Eqn. 1) for methane seepage intensity which weighs in the relative proportion of GDGTs (GDGT-1, -2, and -3) preferentially synthesized by methanotrophic archaea with that of non-methane-related biomarker contribution from planktonic and benthic sources (Crenarchaeol and Cren_isomer) [1]. The MI value ranges from 0 to 1, where a higher value indicates an increased presence of methane-related biogeochemical processes.

$$\text{Methane Index (MI)} = \frac{[\text{GDGT}-1]+[\text{GDGT}-2]+[\text{GDGT}-3]}{[\text{GDGT}-1]+[\text{GDGT}-2]+[\text{GDGT}-3]+[\text{Cren}]+[\text{Cren}']} \quad (1)$$



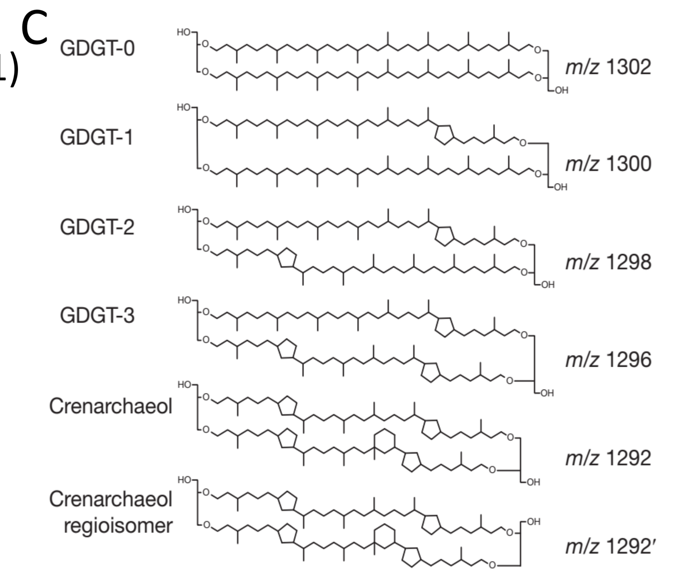


Figure 1: A) Study Area: Site 1230, of ODP Leg 201 (Peru Margin) is drilled at a water depth of 5086 meters below sea level B) Methane and sulfate concentration profile from porewater showing the SMTZ depth at ~8.8 mbsf C) Core structures of the most common isoprenoidal GDGTs with mass-to-charge ratios (m/z)

Study Site and Methods

- Study site (ODP 1230) is an active margin with fluid seepage from below and high phytodetritus sedimentation from the water column. Porewater profile showed a shallow SMTZ at ~8.8 mbsf (Fig. 1).
- We focused the top 22 mbsf with a 50cm depth interval for the study. Higher depth resolution was adopted for depths of interest, especially around the SMTZ depth.
- GDGT analysis was performed through a high-resolution UPLC approach using two silica columns [2] and Orbitrap Fusion Mass Spectrometer. A single-silica column approach was performed for comparison.

Results and Discussion

- Overall, GDGT-O and Cren had the highest average distribution (Fig. 2)
- GDGT-1 and -2 showed higher abundance at the SMTZ (8.7 and 8.8 mbsf, Fig. 2)
- GDGT0/Cren ratio < 2 throughout the sediment column suggests limited GDGT contribution from methanogens
- UPLC approach enabled separation of GDGT compounds and their isomers (Fig. 3)
- GDGT-1 and -2 showed four and GDGT-3 showed six potential isomers (Fig. 3)
- GDGT-1a, -2a, and -3a peaked at the SMTZ and were almost absent at other depths (Fig. 3)
- MI values were highly distinguishable when all GDGT isomers are considered as one pool and when only the GDGT-1a, -2a, -3a isomers are considered (Fig. 4)
- GDGT-1a, -2a, and -3a are potentially sourced from ANMEs

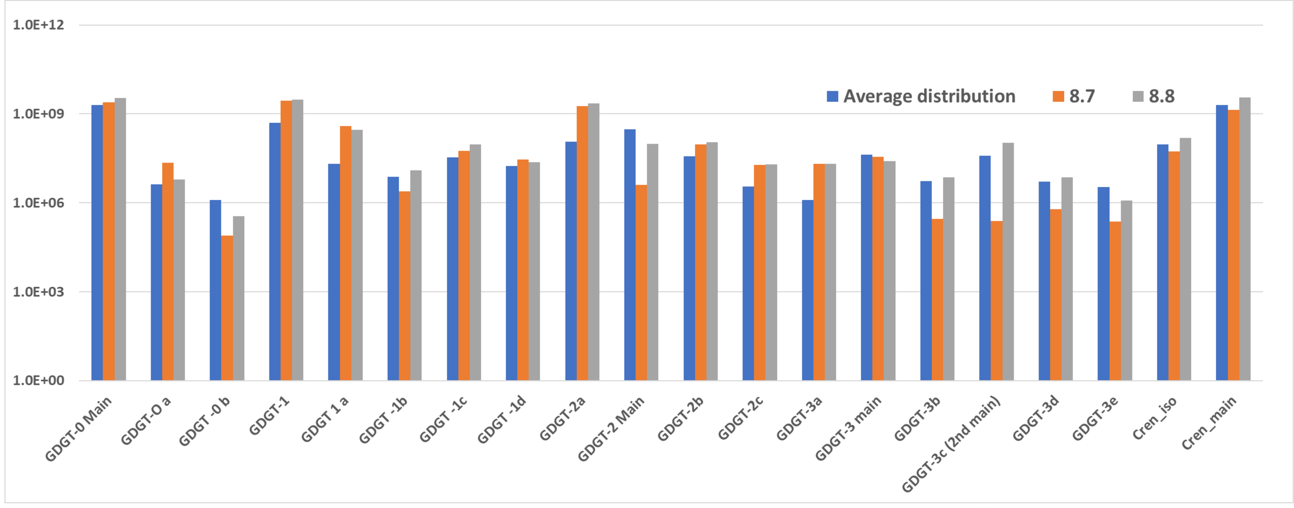
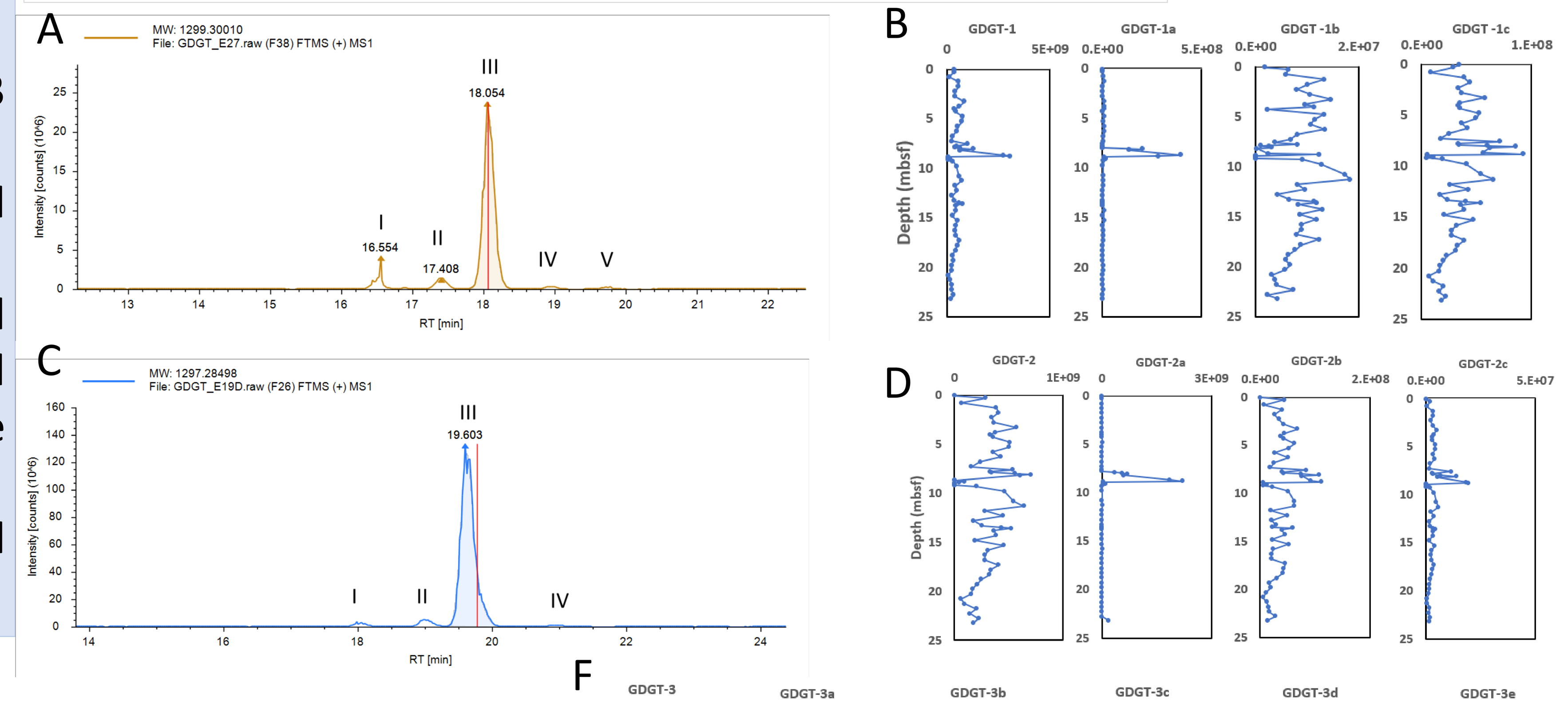


Figure 2: Average distribution of studied GDGT compounds through the sediment column compared with their distribution at SMTZ depths (8.7 and 8.8 mbsf)



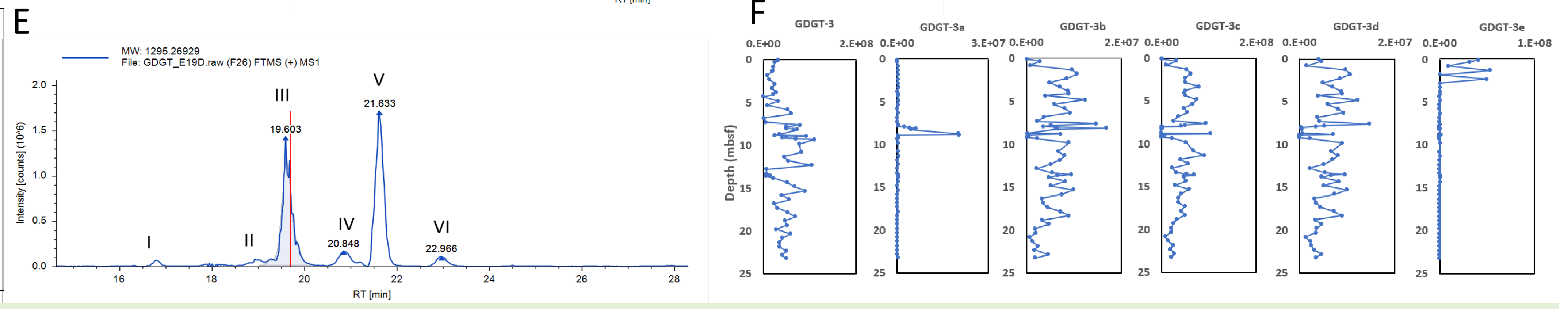


Figure 3: Observed GDGT isomers with their retention time A) GDGT 1 isomers and B) depth-wise distribution. C) GDGT 1 isomers and D) depth-wise distribution. E) GDGT 1 isomers and F) depth-wise distribution.

Summary and Future works

- Effectively high-resolution approach that can distinguish GDGT isomers
- Evidence for novel Isomer patterns of GDGT structures from ANMEs
- Potential to refine MI and other GDGT based paleo-proxies like TEX86
- Future steps involve
  - Compound specific carbon isotope analysis to verify methanotrophic sourcing
  - structural characterization of these isomers
  - Examining the presence/absence of these isomers in other sites with and without methane flux

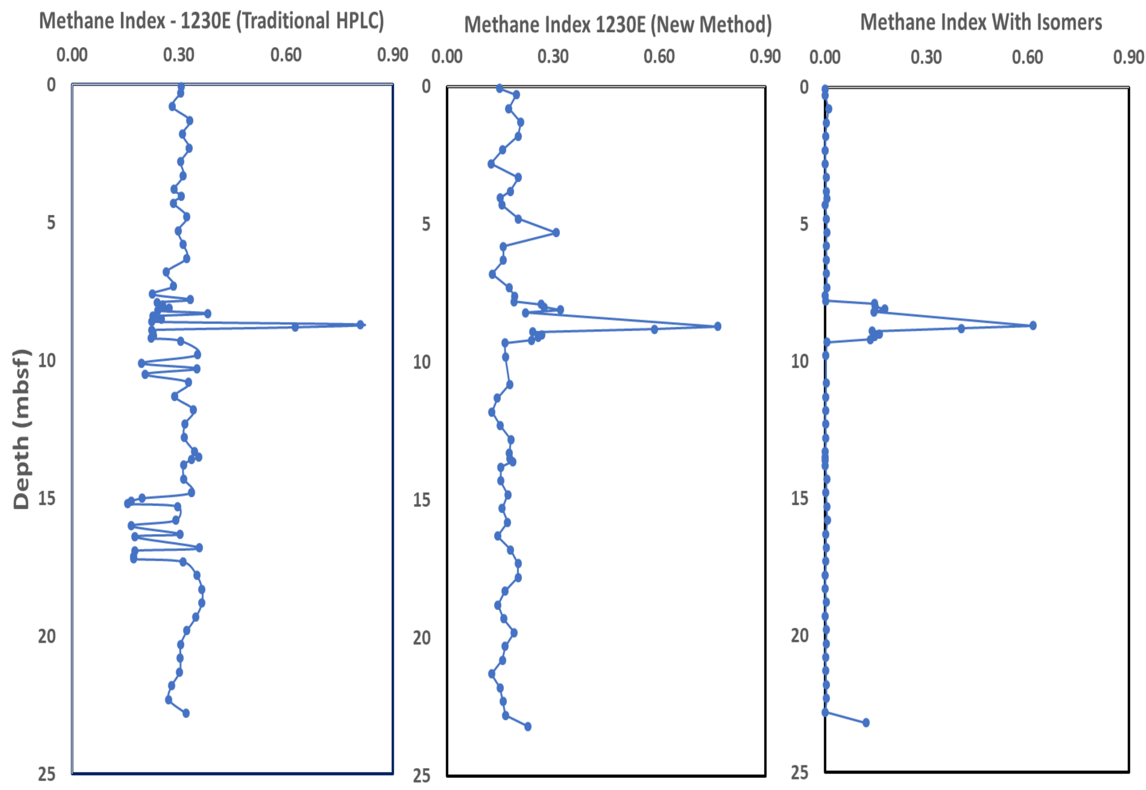


Figure 4: MI values with depth through A) traditional method using single silica column B) two silica columns and C) two silica columns and by accounting only ANME-specific isomers to Eqn. 1

Acknowledgement and References

International Ocean Discovery Program is acknowledged for providing the samples and porewater data.

[1]. Y. G. Zhang et al. (2011), Earth and Planetary Science Letters 307, 525-534
[2] E.C. Hopmans et al. (2016), Organic Geochemistry 93, 1-6.