

Sedimentary Marine Organic Matter Diagenesis under Methanogenic Conditions: A New Model for Biogenic Gas Quantification*

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Abstract

After its deposition on the sea floor, sedimentary organic matter (SOM) is subjected to intense diagenesis that affects both its quality and concentration in the first hundred meters of sediment. This alteration is due to changes in physicochemical conditions of the sediment and also to the activity of microorganisms growing within the porous medium. Methanogenesis is the final step of this degradation provided by Archaea that produce methane (CH₄) as a waste. The study of methanogenesis in sediments has so far been conducted mainly through thermodynamic calculations and analysis of chemical species dissolved in pore waters, including CO₂ and CH₄. It has been shown that these methods had large errors due to losses occurring during the handling of cores. There are also numerous studies on the rate of methanogenesis through measurements of carbon isotopic fractionation by methanogens and laboratory simulations. Despite this abundant literature, the precise effects of methanogenesis on SOM are poorly understood and interactions with the mineral medium are virtually unexplored, due mainly to the highly insoluble character of the SOM and the lack of appropriate structural analysis tools.

The aim of this study is to describe the early diagenesis of a recent marine SOM under methanogenic conditions so as to determine the most bio-reactive structural motifs (whose concentration decreases with depth) and those with slower degradation kinetics, considered refractory. Once the labile compounds and the process and stoichiometry for their degradation are established, we will be able to determine the total volume of CH₄ produced using the existing equations for methanogenesis.

Method

To achieve this goal we choose a natural sedimentary series from a core drilled off Namibia during the course of Leg 175 of the Ocean Drilling Program (ODP; Wefer et al., 1998). This area is known to be one of the most productive regions in the world and is characterized by organic-rich sediments with high organic carbon content (3-4%; Wefer et al., 1998; Giraudeau et al., 2002). This site appears to be suitable for “natural diagenetic experiments”, allowing us to not only characterize the impact of methanogenesis on natural organic matter but also to apprehend the interactions with the mineral matrix and the changes in the geological parameters (temperature, porosity, permeability, etc.).

Twenty samples are selected from ODP Site 1082 (1 every 20 m) to a depth of about 400 meters below sea floor (mbsf) at which CH₄ is still abundant in pore waters (around 10,000 ppm). Rock-Eval pyrolysis and elemental analysis are conducted on the isolated insoluble organic matter (kerogen) and the results confirm the marine and very homogeneous aspect of the organic material at this site (Twichell et al., 2002). They also showed that methanogenesis was responsible for a steady diminution of the oxygen index (OI) from 110 to 70 mg of CO₂ per g of TOC and the O/C atomic ratio from 0.3 to 0.2 during burial.

The kerogen, consisting of bio-macromolecules, is refractory to molecular characterization and can only be characterized through global methods such as elemental analysis, nuclear magnetic resonance (NMR) and infrared spectroscopy. Hence, a major challenge in the organic geochemistry field is to push the boundaries of structural characterization for the SOM. To overcome that problem we propose a mild closed system pyrolysis that leads to the cleavage of weak bonds linking polar molecules to the insoluble bio-macromolecule. The soft pyrolysis thus makes these polar molecules extractable in organic solvents with minimum alteration of the chemical functional groups they carry. It also has the benefit not to be selective regarding the nature of the functional group and allows the release of a significant diversity of polar molecules. However, the pyrolysis method can lead to the alteration of the functional group and the cleavage of the hydrocarbon backbone if the temperature is too high. This parameter must be determined with precision; it has to be high enough to release the polar compounds connected to the SOM, but not too high so as not to degrade its structure. We determine that 200° C was the most adequate temperature for our samples.

Results and Conclusions

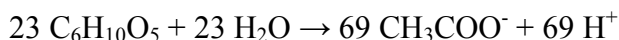
Elemental analyses performed on the pyrolysates validate the crucial aspect of the mild pyrolysis at 200° C. It shows that the O/C atomic ratios become constant around a value of 0.15 ([Figure 1](#)). The difference between the O/C atomic ratios of the kerogens and those of the corresponding pyrolysis residues becomes vanishingly small with depth. The oxygen-rich released products thus bear the signature of the bio-reactive molecules. The latter are successfully extracted under reflux in dichloromethane (DCM) and the yield of the extractions shows again a decrease from around 70 to 30 mg per gram of kerogen ([Figure 1](#)).

Submitting kerogens and pyrolysis residues to ¹³C NMR, we obtain a quantitative distribution of the organic carbon in aliphatic, aromatic and functional structures, as well as a mass balance of the carbon released during the pyrolysis. This mass balance, associated with a structural characterization of the pyrolysis products, allows us to quantitatively target the molecules degraded during the methanogenesis.

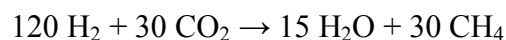
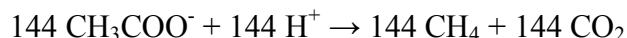
We identify two degradation zones. The first one commencing from the top of the methanogenesis window, at 23 mbsf (depth at which sulfates give way to CH₄ in pore waters) to 100 mbsf, shows a marked decrease in the carbohydrate content of the kerogen. This decrease is characterized by an anomeric carbon loss of 1.46% of the total carbon given by the NMR and confirmed by the yield of CO₂ during the pyrolysis. Then, the degradation of fatty acids takes over and increases exponentially from 100 mbsf. The carbonyl carbon loss is about 1% of the total carbon and using gas chromatography-mass spectrometry (GC-MS) we show that this loss is mainly in the form of C₁₀ normal fatty acids.

To model those changes, we use a conceptual Type II kerogen molecule with a global molecular formula of C₁₅₀₀H₂₁₇₅O₄₂₀ leading to the same O/C and H/C atomic ratios as the kerogen at the top of the methanogenesis window (0.28 and 1.45 respectively). We can now degrade this kerogen based on the stoichiometry determined analytically and balance equations from the literature. It is known that the methanogenesis reaction is in fact the sum of three reactions: (1) the first one is ensured by acetogenic bacteria that degrade the organic polymers into hydrogen and acetate, (2) hydrogenotrophic methanogens will then use the hydrogen to produce CH₄, and (3) finally the acetoclastic bacteria will use the acetate to produce CO₂ and CH₄.

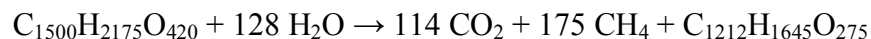
Thus carbohydrates and fatty acids are converted to acetate and hydrogen as follows:



The hydrogen and acetate are subsequently consumed to form CH₄:



The global equation for the degradation of the conceptual kerogen is:



This degradation leaves a residual kerogen with a global formula C₁₂₁₂H₁₆₄₅O₂₇₅ and we validate that it has the same atomic parameters as the natural kerogen at 350 mbsf (i.e. an O/C atomic ratio of 0.22 and an H/C atomic ratio of 1.35).

With the average total organic carbon at the top of the methanogenesis window being 3%, 1 m³ of sediment contains 84 kg of organic matter, i.e. 3.12 moles. From our global equation of methanogenesis we infer that 13 m³ of CH₄ are produced per 1 m³ of sediment at 350 mbsf. Methanogenesis is thus responsible for a consumption of about 20% of the initial organic carbon, but the high O/C ratio (0.22) and the presence of a large pool of fatty acids at 350 mbsf shows that the kerogen can still support further degradation.

References Cited

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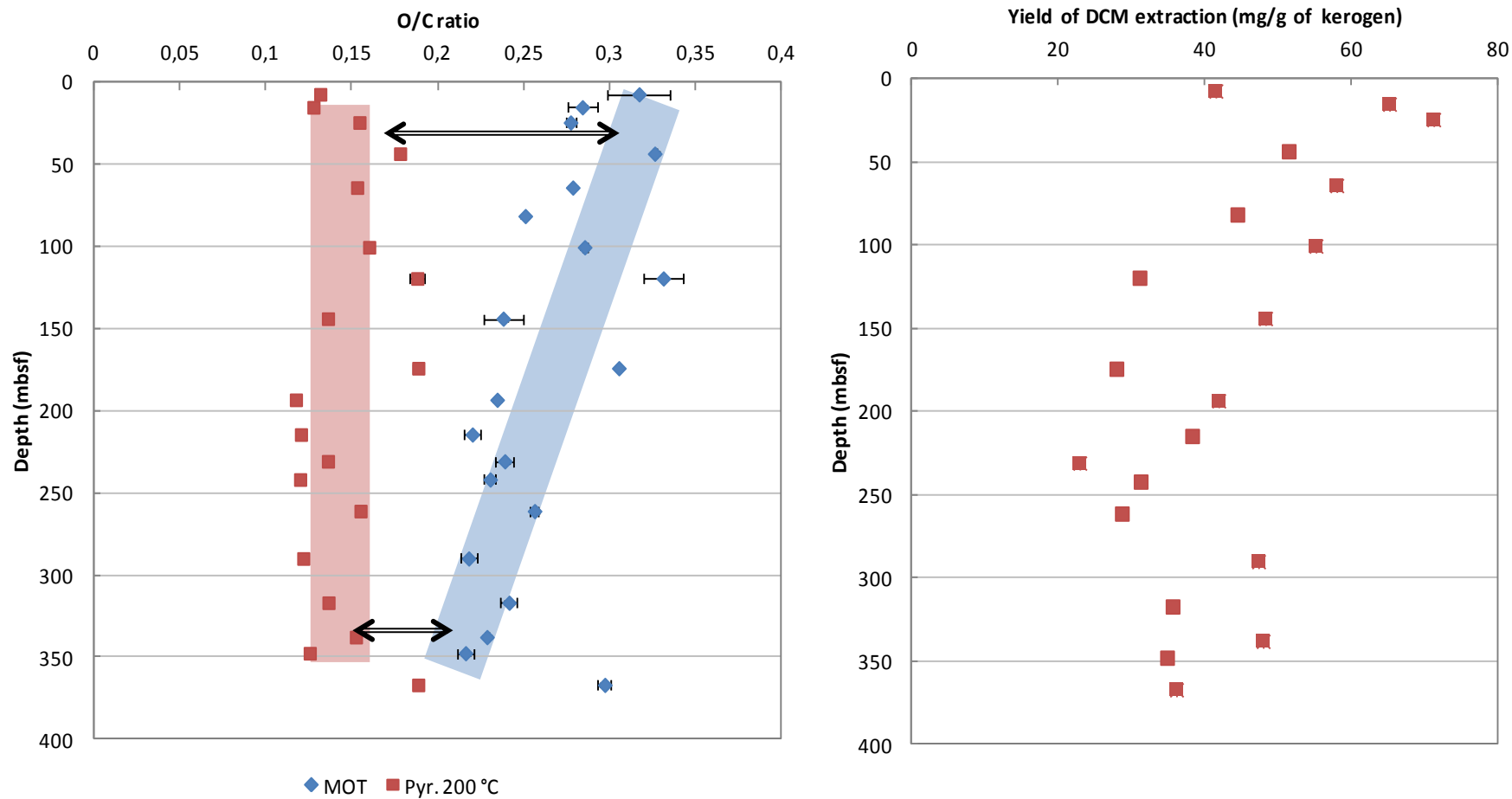


Figure 1. (left) Distribution of the O/C ratios versus depth for the kerogen and the pyrolysis residues. (right) Yield of the DCM extraction of the pyrolysates versus depth.