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Methanogenic microbial community of the Eastern Paris Basin: Potential for energy production from organic-rich shales

Margaux Meslé [a], Charlotte Périot [a], Gilles Dromart [b,c], Philippe Oger [a,*]

[a] CNRS UMR 5276, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon, France
[b] Université de Lyon, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon, France
[c] Tharsis-Energy, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon, France

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ABSTRACT

Shallow, thermally immature organic-rich shales represent considerable resources in the Paris Basin (France). We investigated the presence of methanogenic consortia (i.e., syntrophic bacteria and methanogens) in the Lower Toarcian Paper Shales formation, to link geochemical and lithological properties of the rocks to the spatial distribution of microbial communities. The presence of methanogenic microbial populations, demonstrated via their growth in enrichment cultures, occurs throughout most of the rock layers, and may be explained by the transport of organics and microorganisms within the formation. The enriched consortia were able to utilize the organic matter of the rock as sole carbon source in microcosm, indicating a strong potential of these microbial communities for methanogenesis in situ.

1. Introduction

Thermally immature, shallow organic-rich shales represent worldwide resources for unconventional gas generation. Microbial methane (CH_4) is known to occur in situ in these particular substrates, as evidenced by its $\delta^{13}C$-depleted isotopic signature (Martini et al., 1996, 2003, 2008; Shurr and Ridgley, 2002) and its high proportion compared to C2–C5 hydrocarbons (Martini et al., 2008; McIntosh et al., 2008; Shurr and Ridgley, 2002; Strapoc et al., 2011). Active microbial methanogenesis in organic-rich shales was mostly detected along the shallow margins of the sedimentary basins (Shurr and Ridgley, 2002), which exhibit low organic matter (OM) maturity and active hydrogeological flow systems (Martini, 2005). Shale formations by their low permeability constitute excellent aquitards (i.e., confining layer in which groundwater can be trapped), often located between two aquifers represented by permeable and water-saturated sand or carbonate formations. The distribution of aquifers and aquitards has a major control on fluid migration in sedimentary basins (McIntosh et al., 2008). Meteoric waters allow an increasing dilution of basin brines from the center to the margins, which impacts the yield and pathway of microbial methanogenesis (Martini et al., 1998; McIntosh et al., 2008; Schlegel et al., 2013) as well as the diversity and distribution of methanogenic archaea (Waldron et al., 2007). The microbial mineralization of OM into CH_4 in these shallow biogenic gas systems relies on the cooperation of different groups of anaerobic microorganisms. The fermenting bacteria hydrolyze the complex organic molecules into monomers, further transformed by syntrophs into substrates used by methanogens (Espitalie et al., 1977; Liu and Whitman, 2008; Meslé et al., 2013b; Schink, 1997; Zengler et al., 1999; Jones et al., 2013). Bacterial sequence data obtained from methane- and water-producing wells in the Antrim Shales formation have shown that a variety of fermentative, syntrophic, and homoacetogenic bacteria inhabit the shale (Formolo et al., 2008b; Kirk et al., 2012; Martini, 2005; Waldron et al., 2007). As observed in other organic-rich environments (e.g., oil and coal) (Meslé et al., 2013b), the bacterial diversity is dominated by various genera belonging to the phyla Firmicutes, Bacteroidetes and Proteobacteria. Archaeal sequences collected from the same wells show that these syntrophic bacteria are associated with three main classes of methanogens, with a majority of Methanomicrobiales and Methanosarcinales, and a lower proportion of Methanobacteriales (Kirk et al., 2012; Martini, 2005; Waldron et al., 2007).

A few studies have shown that microbial communities associated with immature source rocks are able to utilize the dissolved organic matter (DOM) present in organic-rich shales as source of organic carbon and electron donors (Fredrickson et al., 1997; Krumholz et al., 1997, 1999, 2002; Takai et al., 2003). In the Antrim Shales of the Michigan Basin, shale-derived DOM is degraded by microbial communities for growth with methanogenesis as the terminal electron acceptor process (Gieg and Suflita, 2002; Krumholz et al., 2002; Martini et al., 2008; Rabus et al., 2011; Widdel and Rabus, 2001). Similar conclusions could be drawn for methanogenic consortia of the Cretaceous shale and sandstone formations of the southern San Juan Basin (New Mexico): archaeal

* Corresponding author.

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methanogens and bacterial sulfate-reducers are spatially organized in different sections of the rock (Krumholz et al., 1997). Bacterial acetogens and sulfate-reducers were isolated at the shale-sandstone boundary and active sulfate reduction is located essentially in the sandstone (Krumholz et al., 1997), while active methanogenesis and methanogens identified as Methanosarcinaceae were located inside the shale (Takai et al., 2003). Low microbial populations and activities in the compact shales in comparison to the more permeable sandstones directly result from restrictive pores that affect bacterial mobility, limit nutrients transport, and lead to reduced biodiversity (Fredrickson et al., 1997; Rebata-Landa and Santamarina, 2006). These observations clearly demonstrate the structuring impact of the geochemistry and lithology of the rock on colonizing microbial communities.

The present study focuses on the shallow, immature, and organic-rich Paper Shales ("Schistes Carton") of the Eastern Paris Basin (Lower Toarcian, ca. −180 My). The Paper Shales formation constitutes an aquitard, confined between the limestones of the Dogger aquifer and the carbonate/sandstone of the Trias aquifer. Although microbial generation of methane has not yet been formally proven in the organic-rich Paper Shales, this formation is structurally similar to the aquitard/aquifer system of the Antrim Shales, and thus represents a good candidate for methanogenesis. Preliminary exploration of the Paper Shales formation showed that methanogen cell numbers remain below the detection limit of molecular approaches, but could be detected after cultivation in microcosm (Meslé et al., 2013a). In the present study, we investigated the presence of methanogenic consortia by enrichment from different depths in the Paper Shales formation, and aimed at connecting the spatial distribution of methanogens with environmental factors (e.g., depth, general lithology, carbon substrate of the source rock). In contrast to the Antrim Shales, we cannot identify a strong structuring effect of the lithology on the vertical distribution of methanogens in the Paper Shales, which may reflect the importance of water circulation at the basin margin, providing a beneficial environment for methanogenesis.

2. Materials and methods

2.1. Coring and field sampling

The target source rocks belong to the Lower Jurassic black shales (Paper Shales) of the eastern Paris Basin (margin), known as type II kerogen-rich shales (Tissot et al., 1974; Vandenbroucke and Largeau, 2007). Rotation drilling (diameter of 89 mm) with surface waters was operated in the field to a depth of 31 m at Entrange (Moselle, North-East of France, 49°25′04.7″N, 06°06′14.17″E, Z = 261 m, Fig. 1). The cutting head has been fitted with switchable core catchers in order to avoid sample contamination. Mud formed on the surface of the core during the drilling was removed prior to geochemical and biological sampling. Rock samples for geochemical analysis were collected on site every ten centimeters along the core, and 13 samples of variable thickness (from 1 cm to 4 cm) and depth were chosen for biological experiments (microcosms). After sampling, cores were stored in sealed plastic bags in anaerobiosis to avoid oxidation.

2.2. Geochemical analysis of core samples

Geochemical characterization of the OM was performed by Rock-Eval 6® pyrolysis (Behar et al., 2001) at the French Institute of Petroleum (IFP Energies nouvelles, Rueil-Malmaison, France) using 100 mg of pulverized source rock per analysis. Data included total organic carbon (TOC), thermal maturity (T_{max}), free hydrocarbons (S1, or already generated oil in the rock), oil potential (S2, or hydrocarbons to be produced by thermal cracking), hydrogen index (HI, or hydrogen richness), and oxygen index (OI, or oxygen richness) values.

2.3. Microcosm setup

Microcosms were prepared on site in a mobile laboratory, with 13 freshly collected rock samples selected based on their lithology. We tried to maximize source rock differences, but samples with the same facies were also collected from various depths to evaluate the influence of environmental parameters on the microbial distribution and response to biostimulation (i.e., organic carbon addition, Meslé et al., 2013a). To avoid drilling fluid contamination, the outer layer of the core was removed. Samples were taken from the innermost portions in zones devoid of fractures and then ground to powder. Two microcosms per sample were prepared from 4 g of pulverized shale and 25 ml of CP1 medium (described in Meslé et al., 2013a), in 50 ml serum bottles sealed with a rubber cap and a metal ring Before use, 0.5 ml of both Wolfe vitamin and trace mineral solutions (Wolin et al., 1963) from anaerobic sterile stocks were added to CP1 medium. Anoxic conditions in the vials were obtained by

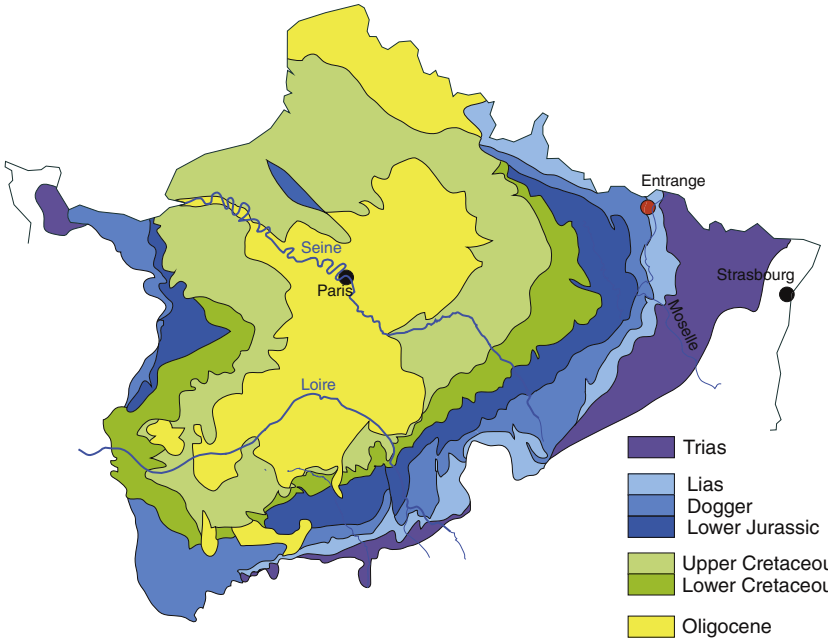

Fig. 1. Simplified geological map of north-eastern France showing the location of the sampling site (Entrange) in the Moselle region.