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Generation of Methane by Biostimulation in Shallow, Kerogen-Rich Shales

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Unconventional natural gas has been one of the main targets of Exploration and Production activities for the last decades. The term refers to gas extracted from reservoirs of very low permeability. Shale gas is produced from fine-grained sediments that are typically rich in organic carbon [1]. In addition to free gas stored in pores and fractures, gas shales also contain sorbed gas associated with the organic compounds and in solution. Economic gas shale plays prove both a hydrocarbon source rock for the source of methane (thermogenic and/or biogenic), and a brittle lithology which contains natural and induced fractures. Microbial production has been documented to be the dominant source of methane in shallow gas shale plays (e.g. 500 m, northern producing trend of the Antrim Shales in the Michigan Basin, [2] & [3]).

Natural alteration of organic matter into methane by microorganisms in oxygen-depleted subsurface environments is a widespread and common process called *methanogenesis*. The biogenic generation of methane from the molecules of kerogen is achieved by a symbiotic consortium of microorganisms. Syntrophic bacteria of the consortium break down the organic molecules through anaerobic respiration and fermentation into simple, water-soluble compounds (e.g. acetate, CO_2, H_2), which are ultimately transformed into CH_4 by methanogenic archaea [4].

Here we report on stimulation of thermally-immature, type II kerogen-rich shales to produce methane in microcosms when the native microbial population is supplemented with nutrients (a treatment referred to as "biostimulation").

Our experiments aim at understanding the mechanisms of the methane production by stimulated microbial consortia, and determining the parameters that influence the system in order to assess the potential methane production capacity of these rocks. The approach chosen to address these questions is threefold: (i) the quantification and description of the organic matter of the source rock (ii) the quantification of the alteration of the organic matter into methane by the indigenous microbial populations (iii) the quantification and identification of the microbial consortia involved in the methane generation.

The source-rocks of interest are the Lower Jurassic black shales of the eastern Paris Basin (i.e. type II kerogens). Samples were collected through a couple of coredrills. Cultures were realized on-site, using a specifically designed growth medium. Anoxic conditions in the cultures were obtained by atmosphere substitution and the addition of a powerful reducer.

The kerogens from the rock samples were characterized by the Rock-Eval 6® pyrolysis technique [5], and the kinetics of methane production was monitored by gas chromatography (Agilent Technology®). The microbial consortia were monitored using different molecular tracers. Quantitative Polymerase Chain Reaction (qPCR) was used to detect and quantify the genes specific of the different microbial consortia (bacteria, archaea, and, more specifically, methanogens). The spatial and temporal evolution of the consortia was monitored by Temperature Gradient Gel Electrophoresis (TGGE), a molecular fingerprinting method consisting in the separation of different sequences of the same gene, made possible the detection of the different microbial communities or species of the rocks, corresponding to the different sequences. Finally, the microbial diversity of the system was identified by sequencing the diverse DNA fragments obtained with the TGGE. These different results were used to estimate the potential methane gas conversion of the source rock.

Geochemical analyses revealed some heterogeneity of the kerogen-rich shales down the borehole, in terms of petroleum potential (S2), total organic carbon (TOC), as well as hydrogen and oxygen indexes (HI and OI respectively). We were able to detect methane production in the deepest layer of the core after a few weeks (i.e. 64 days) of incubation (see figure below). The presence of methane in the cultures perfectly correlates with the detection of archaea and methanogens by qPCR. The absence of methane in the cultures is correlated with the lack of detection of methanogens in the microcosms. We observed a lag period between the appearance of methanogens and the production of methane (see figure). This period may correspond to the time required for the degradation of complex organic matter into simple, water-soluble compounds by the syntrophic bacteria.

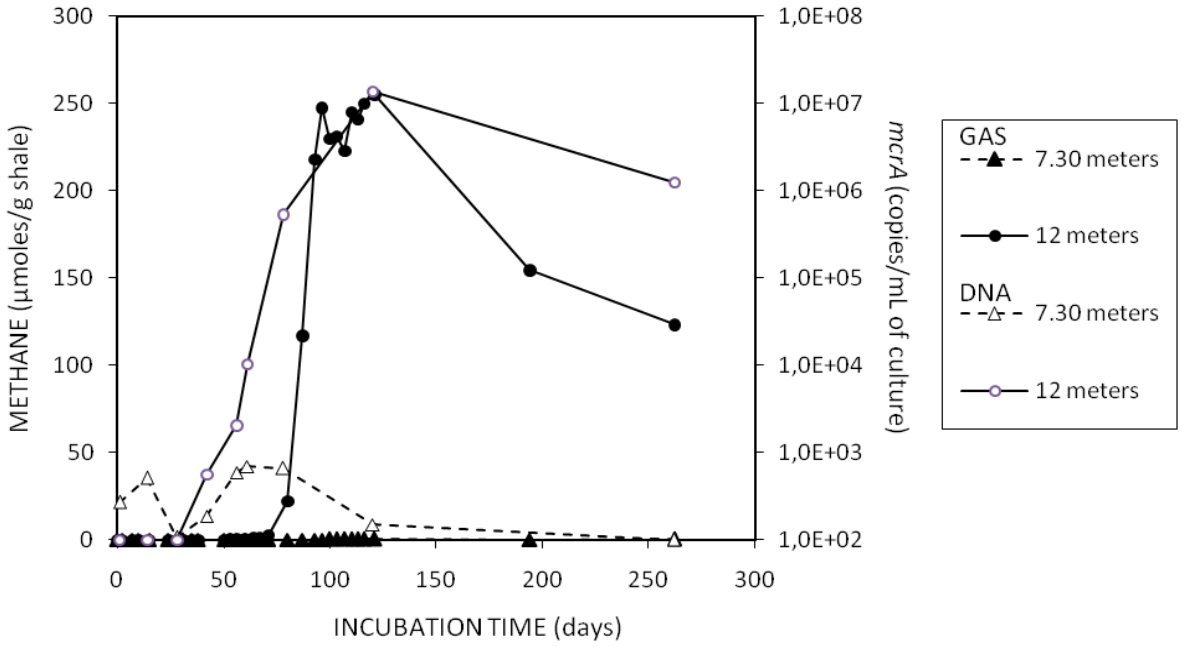

Figure: Methane generated from shale by stimulated native microbial populations. The total number of methanogens was determined by using qPCR targeting the *mcrA* gene (encoding the subunit A of the methyl coenzyme-M reductase) expressed in copies per mL of culture (detection limit 10^2 copies/mL). Two depths of the core are represented: At a depth of 7.30 m (triangles, dotted lines), the methane production and methanogens detection is low, whereas a productive layer with a pervasive presence of methanogens occurs at a depth of 12 m (circles, solid lines).

Our observations indicate that methane can be generated from thermally-immature, type II kerogen-rich shales via biostimulation of indigenous/native microorganisms. Further work using TGGE monitoring will help identify the bacterial, archaeal and methanogen populations involved in the production of methane, and understand their role and complex relationships. The depletion of methane production observed at the end of the incubation, although enough organic matter is still present in the microcosm, might indicate the development of methanotrophic consortia in the microcosm.

Our findings are similar to results obtained from comparable experiments performed on sub-bituminous coals of nonproductive wells [6]. Repeated successes of biostimulation to generate gas from immature source-rocks should prompt tentative implementations of the technique in the field. To generate any microbial gas play, the hydrologic framework is critical for the natural inoculation of the microorganisms, and basins margins, where the organic matter is less mature and the fractures more open, should be targeted.

[1] Schulz, H.-M., B. Horsfield and R.F. Sachsenhofer, 2010. Shale gaz in Europe: a regional overview of current research activites. Geological Society, London, Petroleum Geology Conference series **7:**1079-1085

[2] Martini, A.M., L.M. Walter, T.C.W. Ku, J.M. Budai, J.C. McIntosh and M. Schoell, 2003. Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin. AAPG Bulletin **87:**1355-1375

[3] Martini, A.M., L.M. Walter and J.C. McIntosh, 2008. Identification of microbial and thermogenic gas components from Upper Devonian black shale cores, Illinois and Michigan basins. AAPG Bulletin **92:**327-339

[4] Liu, Y. and W.B Whitman, 2008. Metabolic, Phylogenetic, and Ecological Diversity of the Methanogenic Archaea. New York Academy of Sciences **1125:**171-189

[5] Behar, F., V. Beaumont and H.L. De B. Penteado, 2001. Rock-Eval 6 Technology: Performances and Developments. *Oil & Gas Science and Technology* – Rev. IFP, **56:**111-134

[6] Jones, E., M. Voytec, M. Corum and W. Orem, 2010. Stimulation of Methane Generation from Nonproductive Coal by Addition of Nutrients or a Microbial Consortium. Applied and Environmental Microbiology **76:**7013-7022.