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Modeling of microbial gas generation: application to the eastern Mediterranean "Biogenic Play"

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ABSTRACT

Biogenic gas is becoming increasingly important as an exploration target in the petroleum industry because it occurs in geologically predictable circumstances and in large quantities at shallow depths as free gas or gas hydrates. As accumulations of biogenic gas result in a subtle synchronization between early generation and early trapping, we integrated a macroscopic model of microbial gas generation within a 3D basin and petroleum system forward simulator.

The macroscopic model is based on a microscopic model, which consists in a 1D sedimentary column that accounts for sedimentation, compaction, Darcy flow and Diffusion flow. The organic carbon is the only non-soluble element considered in this version of the model. The dissolved elements are O_2, SO_4^{2-}, H_2, CH_3COOH, and CH_4. Methane is dissolved in water or present as a free phase if its concentration exceeds its solubility at given pressure and temperature. In this microscopic model, the transformation of substrate into biomass is described through a set of logistic equations coupled with the transport equations (advection and diffusion).

Based on the microscopic considerations we developed the macroscopic model of low maturity/biogenic gas generation in which hydrocarbons are generated through first order kinetic reactions at low maturity. This macroscopic model is adapted to petroleum system modeling at basin scale with TemisFlow®, which aims to understand and predict hydrocarbon generation, migration, and accumulation. It is composed of: i) A source rock criteria which allow defining the biogenic gas source rocks potential and ii) A kinetic model of methane generation. The previous model has been successfully applied on different basins such as the Carupano Basin from the offshore Venezuela, the Magdalena Delta (offshore Colombia) and the offshore Vietnam where direct observations of low-maturity gas were available. Furthermore, it has been applied in the offshore Lebanon in order to check the viability of a biogenic gas system.

KEYWORDS **Biogenic Gas. Basin Model. Petroleum System. Eastern Mediterranean.**

INTRODUCTION

Biogenic gas is becoming increasingly important as an exploration target in the petroleum industry because it occurs in geologically predictable circumstances and in large quantities at shallow depths as free gas or gas hydrates. Furthermore, about 20% of conventional gas is interpreted to be microbial in origin (Rice, 1992).

As accumulations of biogenic gas result in a subtle synchronization between early generation and early trapping, we need to integrate a model of microbial gas generation within a 3D basin and petroleum system forward simulator.

Microbial gas production is a complex process that should be described at the microscopical scale. This is generally achieved in the realms of food microbiology and of waste treatment but not for the models that are developed at basin scale (*e.g.* Pelet, 1984; Soetaert *et al.*, 1996; Arndt *et al.*, 2006; Wallmann, 2006; Burdige, 2011; Pastor *et al.*, 2011; Arning *et al.*, 2012, 2013a, b), which do not account explicitly for the populations of microbes that are involved in the biogeochemical processes. The microscopic model should be up-scaled in order to be usable at geological basin scale by coupling it with the 3D basin and petroleum system forward simulator.

Thermogenic gases are generated from kerogen and oil by cracking at high temperature. Methane also forms as a by-product of anaerobic microbial metabolism. Pure microbial gases (biogenic gases) are characterized by exceptionally low concentrations of ethane and heavier hydrocarbons and isotopically light methane carbon (Whiticar, 1994).

The conditions leading to the formation of microbial gas are well established. Methanogen microbes require organic matter and anoxic sulfate-free conditions, at temperature less than the assumed pasteurization temperature at about 75ºC (Claypool and Kaplan, 1974; Rice and Claypool, 1981; Zhang and Chen, 1985; Rice, 1992; Wilhelms *et al.*, 2001). The organic matter may be of two origins: i) remains of organisms accumulated within the sediments (“primary” biogenic methane quickly generated after the sedimentation close to the surface), ii) or mature thermogenic oils (“secondary” biogenic methane produced by the biodegradation of deeper oil pools). This paper is dedicated to the first source of biogenic gas.

The sedimentary organic matter is mainly produced in the euphotic zone of the ocean. For example, Martin *et al.* (1987) estimated that the primary production of ocean is around 130g C $m^{-2}y^{-1}$. Part of this primary production (~14%, Martin *et al.*, 1987) passively sinks out the euphotic zone and is progressively decomposed consuming the dissolved oxygen. The sinking organic carbon flux is then a decreasing function of depth. The same authors derived the following normalized power function to compute the organic carbon flux: $F= F_{100}\ (Z/100)^{b}$ with F_{100}= 1.53mol C $m^{-2}\ y^{-1}$ and b= -0.858. As a result, only few percent of the primary production reaches the sea bottom and is buried with the sediments. Using the previous equation, the Sea Bottom Carbon Flux (SBCF) below 300m of water is estimated to be 0.6mol C $m^{-2}y^{-1}$ or 7t C $m^{-2}My^{-1}$.

Once buried in the sediments, microbes (note that the term “microbes” is used here to described bacteria, archaea and cyanobacteria) quickly breaks down the less resistant molecules, such as the nucleic acids and many of the proteins. Heat and pressure convert the preserved organic matter into a substance called humin or protokerogen, to form a kerogen. Time and temperature convert kerogen into petroleum.

Thus part of the organic matter in the sediments is preserved from microbial alteration. Various mechanisms of preservation have been considered such as: geo-polymerization or humification, selective preservation of refractory bio-macromolecules, physical protection of the organic matter by organic or inorganic (*e.g.* clays) matrices (see Burdige, 2007 for a detailed discussion). The resistant organic matter will be grouped together into the protokerogen. The remaining part of the organic matter will compose the hydrolysable fraction of the organic matter. The relative ratio of the hydrolysable fraction (also called “labile” fraction) of the organic matter has been estimated to 30–40% (Burdige, 2007); 30% based on Sulfur-Carbon budget (Clayton, 1992); 40% (Huc *et al.*, 1978; Huc, 1980). In this paper, the TOC (Total Organic Carbon) refers to the total organic carbon fraction including the resistant and the labile fraction. The HOC (Hydrolysable Organic Carbon) quantifies the labile fraction.

Microbes are intimately involved with diagenetic processes in marine sediments, although their role has yet to be detailed completely, especially in sediments far below the sediment–water interface. Microbes, through their ability to produce enzymes (Wetzel, 2001), are known to catalyze many chemical reactions in marine sediments, degrading and modifying deposited organic matter and contributing their own biomass to the pool of organic matter preserved in the geological record. Microbial activity is known to be most intense in surface sediments and declines with increasing depth below the surface layer. However, microbial activity in deep subsurface horizons may still have a major effect on diagenesis because of the long time scales involved in the geological evolution of marine sediments.

During the Deep Sea Drilling Project (DSDP) 96 program, Whelan *et al*. (1986) conducted the first search for subsurface bacterial activity in samples taken from 4 to 167mbsf in the Gulf of Mexico. Results from analyzing pore waters and from culturing sediments samples suggested that bacterial activity probably was present at depth. A more extensive program of microbiological sampling was undertaken during Leg 112 in the Peru margin area (Cragg *et al*., 1990). These latter studies produced unequivocal evidence that bacteria were present to the maximum depth sampled (80mbsf), including a variety of viable forms, some of which were observed as undergoing cell division.

Köchling *et al*. (2011) investigated the composition of the microbial community inhabiting the anoxic coastal sediments of the Bay of Cadiz (southern Spain). The total cell count was 1–5 10^8cells/g sediment and, the proportion of Bacteria to Archaea was about 70:30. The analysis of gene sequences revealed a wide spectrum of microorganisms (more than 100), which showed high similarity to microorganisms living in marine sediments of diverse geographic origin.

Clayton (1992) proposed a characterization of biogenic gas basins in function with the geothermal gradient and the sedimentation rate, which is a key control: too slow, and most of the Organic matter is oxidized near the surface; too fast, and the microbes reach the pasteurization zone too quickly.

In a first part, the model discussed develops a microscopic model, in which the transformation of substrate into biomass is described through a set of logistic equations coupled with the transport equations (advection and diffusion).

In a second part, based on the microscopic considerations, the model develops a macroscopic model of low maturity/biogenic gas generation in which hydrocarbons are generated through first order kinetic reactions at low maturity. This macroscopic model has been implemented in TemisFlow®.

In the third part, the macroscopic model has been applied in Offshore Lebanon in order to check the viability of a biogenic gas system.

PART 1: MICROSCOPIC MODEL OF MICROBIAL METHANE GENERATION

Model description

The microscopic model consists in a 1D sedimentary column that accounts for sedimentation, compaction, Darcy flow and Diffusion flow. It is particularly dedicated to the study of the evolution of the sedimentary organic matter in the first hundred meters below the water–sediment interface, over a period of time of a few hundreds of thousand years. The organic carbon is the only non-soluble element considered in this version of the model. The dissolved elements are O_2, SO_4^{2-}, H_2, CH_3COOH, and CH_4. Methane is dissolved in water or present as a free phase if its concentration exceeds its solubility at given pressure and temperature.

Like other living organisms, microbes require for life and reproduction (Sherr and Sherr, 2000): i) energy, ii) elements for biosynthesis (C, N, P, S, Fe, Mn…) and iii) electrons for producing organic structures.

The energy is provided through redox reactions that could be described as follows (*e.g*. Hedin *et al*., 1998).

$$OM + B_{ox} \rightarrow OM' + B_{red} + \Delta G \qquad (1)$$

Where Organic Matter (OM) is the carbon source: organic matter or CO_2 (electron donor); B_{ox} is the electron acceptor (*e.g*. O_2, SO_4^{2-}); OM' is a degraded form of the organic matter; B_{red} is the reduced form of B; ΔG is the free energy that can be used by the microbes.

The reactions accounted for in this first version of the model are (see Figure 1):

i) The aerobic oxidation of the OM into CO_2
ii) The anaerobic sulfate-reduction of the OM, the acetate, and methane into carbon dioxide and sulfur.
iii) The hydrolysis and fermentation of the OM into acetate, hydrogen and CO_2.
iv) The two pathways for methanogenesis of (1) acetate and (2) hydrogen and CO_2 into methane.

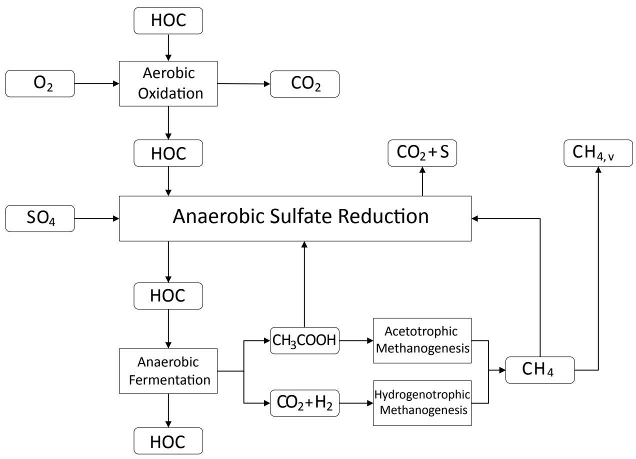

FIGURE 1. Reaction scheme used in the 1D microscopic model.

The substrate (S) and the biomass (B) concentration are supposed to be linked by the following equations (modified from Lawrence and McCarty, 1969; Rosso, 1995; Cherruault, 1998). In case of dissolved substrate, it is assumed that its concentration follows a convective and diffusive mixing process.

$$\begin{cases} \frac{dB}{dt} = a\mu B\left(1-\frac{B}{B_{max}}\right) \\ \frac{dS}{dt}+div\left(S\overline{U}-\frac{D}{\tau}\overline{grad}(S)\right) = -\mu B \end{cases} \quad (2)$$

The term B stands for the biomass concentration [mass/volume], S is the substrate concentration [mass/volume], and "a" represents the growth yield coefficient. The term B_{max} is the maximum concentration of the biomass or the carrying capacity. The term U is the fluid Darcy velocity; Terms D and τ are respectively the diffusion coefficient in water and the tortuosity of the porous medium. The reaction rate μ is given by the Michaelis–Menten formula:

$$\mu = \mu_{max}\frac{S}{K_s+S} \quad (3)$$

Where μ_{max} is the maximum rate of substrate utilization per unit weight of micro-organisms [1/time], and K_s is the Monod coefficient equal to the substrate concentration when dS/dt is equal to one-half of the maximum rate. The temperature dependence of the reaction rate is given by the Rosso *et al*. (1993) relationships (see Figure 2).

In the previous equations, "aμ" is the microbial growing rate and "aμB/B_{max}" is the microbial death rate. It can be easily checked that these two numbers are equal when the microbial population reaches the carrying capacity. These two parameters control the growth and the decrease of the microbe population as shown in the example presented in Figure 3.

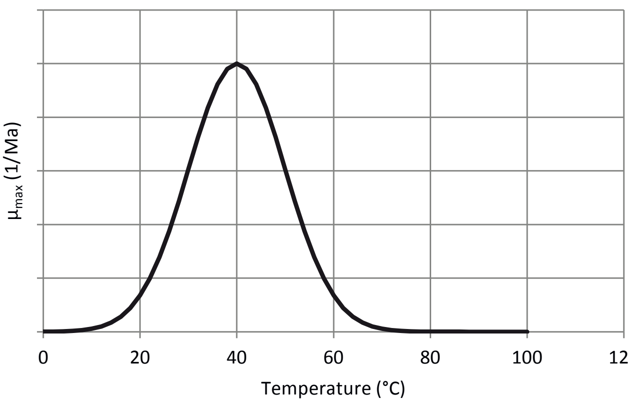

FIGURE 2. Example of temperature dependency for μmax.

Results and discussion

The first results of the model are consistent with the observations in terms of nutrients and microbes concentrations. In the example presented on Figure 4, the oxidation zone is less than 10cm thick, the sulfate reduction zone is some meters thick, and the fermentation zone could be defined between 3–4mbsf (meters below sea floor) and 20–30mbsf. The bottom boundary of the fermentation zone is correlated with the disappearance of the hydrolysable organic matter.

It should be noticed that each equation is defined with free parameters (*e.g*. a, B_{max}, μ_{max}, K_s…) that have to be calibrated in geological situations. This task is under development (Schneider, in prep) using, in particular, the results from the Ocean Drilling Program (ODP)/DSDP programs and some existing lab experiments.

In order to produce methane, the organic matter, once buried, should be preserved partially from the whole oxidation zone. A set of sensitive tests has been carried out in order to evaluate the preservation of the HOC through the oxidation and sulfate reduction zone. The results indicate that the preserved HOC is a function of the initial HOC, and that the preserved HOC increases as the sedimentation rate increases (see Figure 5).

These results suggest that the lower boundary of the Clayton chart (Clayton, 1992) is not universal but is a function of the initial HOC. Another result is that a minimum HOC is required, at a given sedimentation rate, in order to enter the fermentation zone and then to produce methane.

Another set of numerical experiments has been carried out in order to determine the Expulsion Depth (ED). The

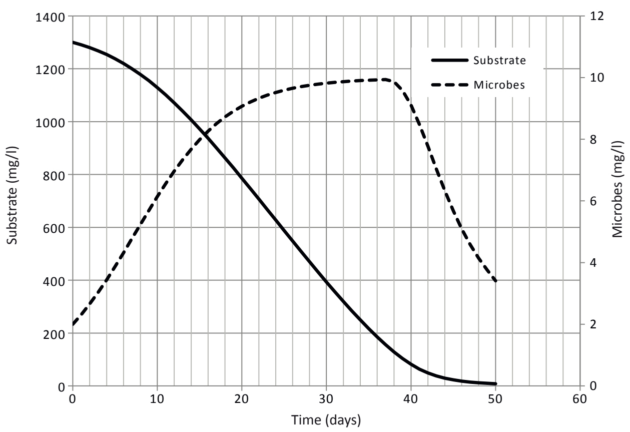

FIGURE 3. Example of simulated evolutions of the substrate content and the microbe population in a waste treatment reactor (data from Converti *et al*., 1998).

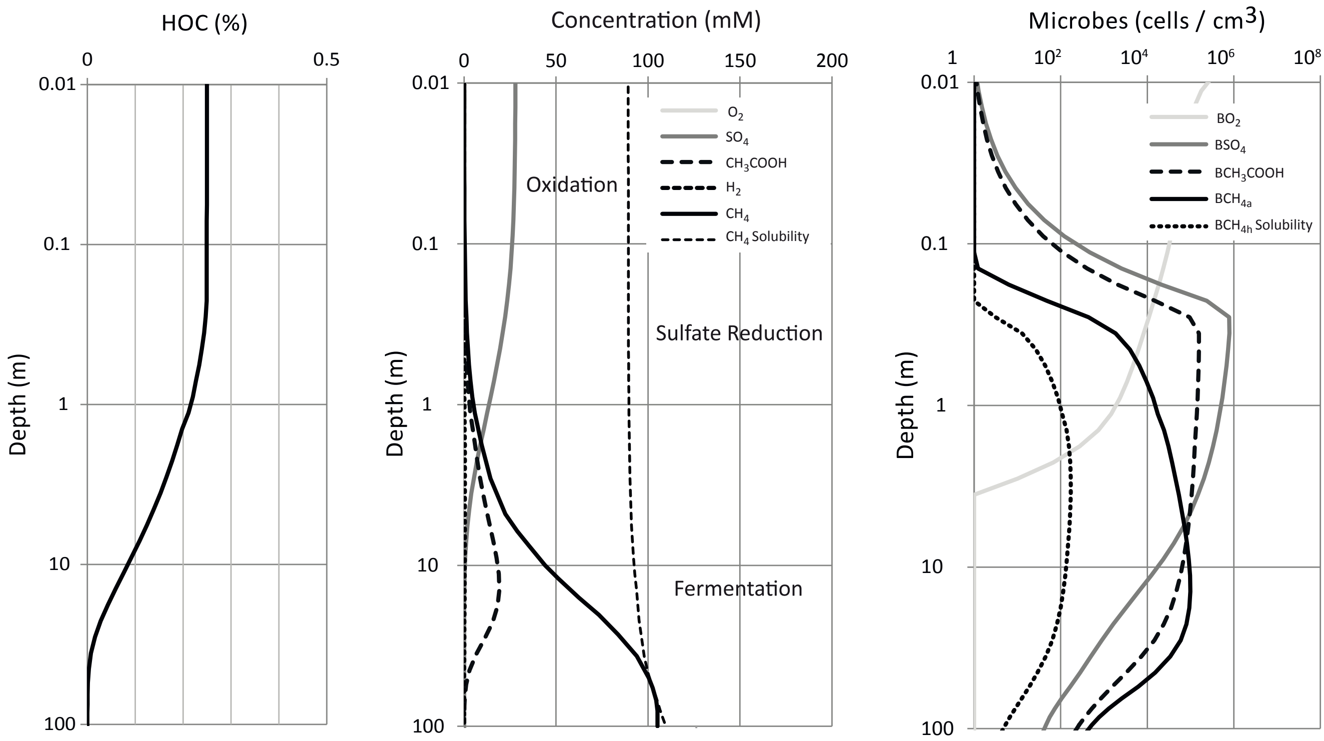

Figure 4. Synthetic example of species and microbes concentrations calculated by the 1D microscopic model.

expulsion depth is defined as the depth where the first buble of free methane is formed. This depth corresponds to the point where the methane concentration in water exceeds the methane's solubility (*e.g*. Lu *et al*., 2008). It is assumed that if the vapor phase appears too close to the surface, a fraction of the methane will be likely lost and not preserved in the geological system. In the example presented in Figure 6, the expulsion depth is around 50mbsf.

The sensitivy analysis shows that the expulsion depth increases as the sedimentation rate increases, and as the initial HOC decreases (see Figure 7): the degazing of methane occurs closer to the surface in case of low sedimentation rate or high TOC (preservation in the geological system less likely).

The tests performed with the model also showed that the production of methane in vapor phase increases as the thermal gradient increases because the methane solubility in water decreases as the temperature increases. These results justify the lower boundary of the Clayton's chart.

PART 2: MACROSCOPIC MODEL OF MICROBIAL METHANE GENERATION

Based on the previous microscopic considerations, a macroscopic model of low maturity/biogenic gas generation has been developed in the "forward" petroleum system modeling tool TemisFlow®. The aim of such model is to understand petroleum system mechanisms at basins scale and through geological times, taking into account a maximum of geological and physical processes, in order to guide exploration strategies and to assess trapped hydrocarbon resources.

In this macroscopic model hydrocarbons are generated through first order kinetic reactions at low maturity. It is composed of:

i) A source rock criteria which allow defining the biogenic gas source rocks potential,

ii) A macroscopic kinetic model of methane generation.

Biogenic gas source definition

"Conventional" thermogenic petroleum system models are designed to geological processes occurring at large scale and over long period of times. Each cell of such models is 10 to one 1000 meters thick and 0.5 to 5km wide, with main time steps generally exceeding 0.1My. Biological processes occurring close to the surface are not directly taken into account. Results of the microscopic model have to be adapted: the objective is to define a biogenic source rock potential which is not only generated but also preserved in the geological system. The amount of HOC

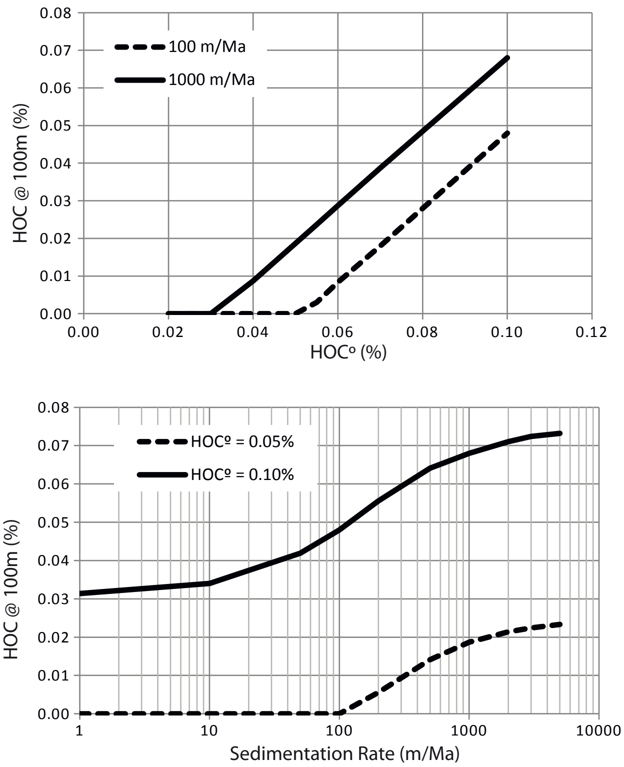

FIGURE 5. Preservation of the HOC through the oxidation and sulfate reduction zone. Left: the preserved HOC is a function of the initial HOC. Right: The preserved HOC increases as the sedimentation rate increases.

consumed by concurrent reactions must be removed from the petroleum system model, as well as the amount of HOC corresponding to the biogenic methane lost at the surface during the early generation. In the same way the potential must be reduced if a fraction of the generation potential is not expressed before the pasteurization.

The sensitivity analysis carried out with the microscopic model indicates that free methane generation is conditioned by the initial TOC, the sedimentation rate and the thermal gradient. A modified Clayton chart (Clayton, 1992) has then been derived in which the lower boundary is now a function of the initial TOC. It should be noted that the upper boundary of the Clayton chart is not justified by the microscopic model in its present version. One reason is put forward: the biogenic potential cannot be fully expressed if the rock crosses too quickly the “biogenic window”, the pasteurization may occur before the complete “consumption” of the HOC by bacteria. Another indirect reason is that the organic matter is often too diluted in case of high sedimentation rate. Further studies are required to valid or invalid this “upper boundary” concept.

For a specific study, the first step is to identify the shaly sediment that contains enough TOC to be considered as a potential biogenic source rock. As explained previously, in the optimal situation the HOC is neither too low (organic matter fully consumed by concurrent reactions) nor too high (liberation of methane in vapor phase too close to the surface). Then, according to the estimated sedimentation rate and the estimated thermal gradient during its deposition, the rock is classified as a good biogenic gas source rock or not, through the definition of a “Biogenic Gas Potential Index”.

For the sake of simplicity when the sedimentation rate and the thermal gradient have some spatial variations, it could be easier to convert the Clayton’s chart into two single heating rate values. In the example presented the lower boundary is equivalent to an heating rate of 7ºC/Ma and the upper boundary equivalent to and heating rate of 18ºC/My (Figure 8). The optimal biogenic window is in between the curves.

Macroscopic kinetic model

In order to get a macroscopic model usable in a basin model; the set of logistic reactions is up scaled into a set of first order kinetics assuming that the biomass is a catalyst (Pfeffer, 1974). It should be noted that the kinetic parameters calibrated from lab experiments are not able to reproduce the nature of the fluids generated at low maturity. Indeed, the kinetic parameters are mainly calibrated with kerogen samples for which Vitrinite Reflectance (Ro) is taken to be approximately 0.6%.

As mentioned before, kinetic parameters are determined in laboratory with samples that are at the limit between diagenesis and catagenesis, at the onset of the oil window hydrocarbon generation. Let us consider a synthetic which is characterized with constant partial HI (Hydrogen Index) of 1mg HC/g TOC for each of the activation energy from 34 to 64kcal/mol (Arrhenius coefficient= 3.1 $10^{15}s^{-1}$). The model performs a numerical maturity experiment on this kerogen in order to place it at a maturity level equivalent to Ro= 0.6%. The results show that all the partial potentials have been totally consumed for activation energy below 50kcal/mol (Figure 9). Considering activation energies between 50 to 54kcal/mol, the partial potentials have been all but partially consumed.

As a matter of fact, for an initial Type III kerogen (“humic” organic matter mostly formed of terrestrial plants: “continental” kerogen), the lowest activation energy that has a positive partial potential is 54kcal/mol (Figure 10, Schneider *et al*., 2012).

By considering the initial Type III kerogen as a starting point and if by observing natural data such as gas compositions, a new set of kinetic parameters may

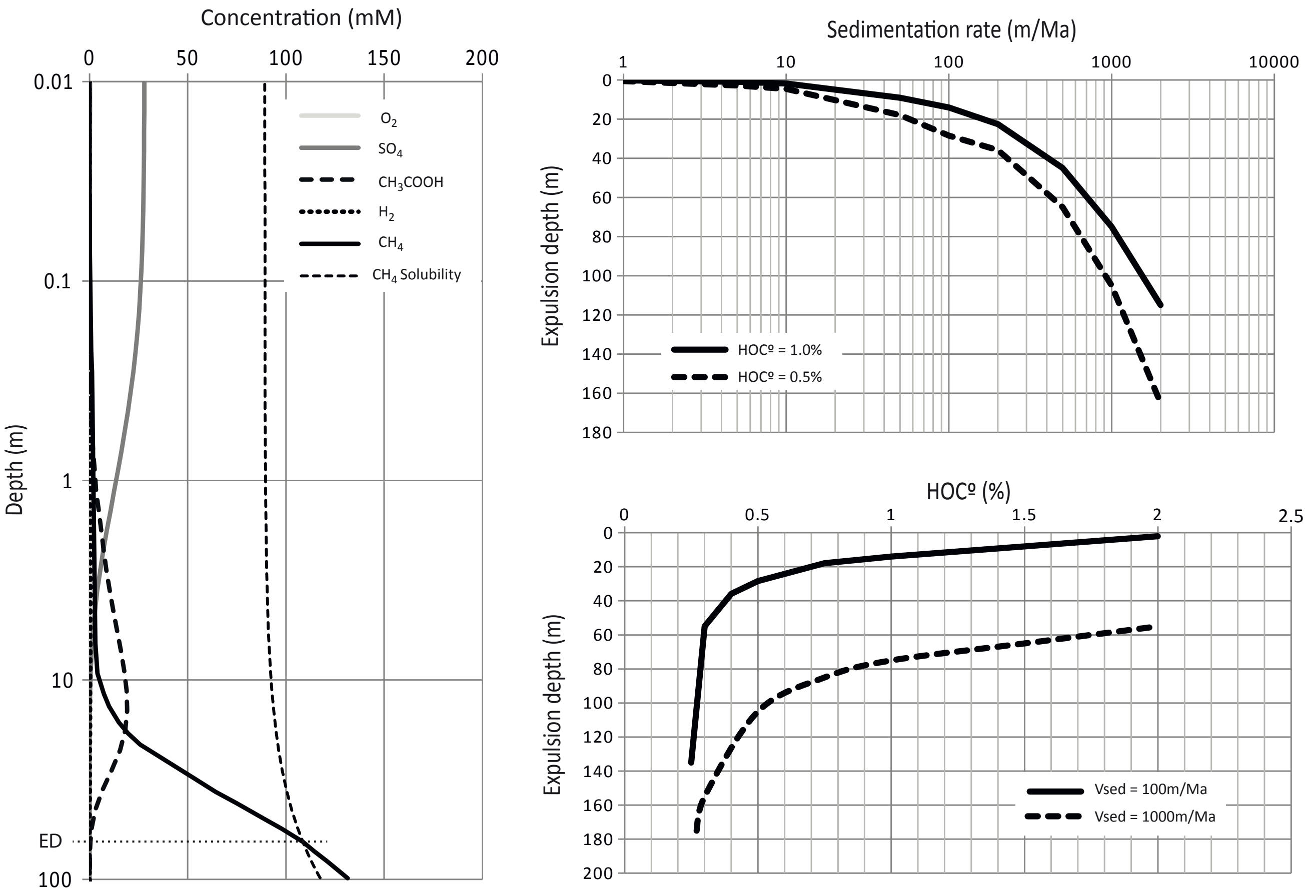

Figure 6. A) The Expulsion Depth (ED) is defined when the methane concentration in water becomes higher than its calculated solubility. B) The expulsion depth increases with the increase of the sedimentation rate. C) The expulsion depth increases when the initial HOC decreases.

be derived to account for low maturities in the gas fields. The derived Type III OM differs from the previous one by a 13% increase of the HI from 235 to 271mg HC/g TOC (Figure 10).

The simulations carried out with new fitted Type III kerogen parameters enables to reproduce quite well the filling of the fields as well as the general composition and state of the hydrocarbons (Schneider *et al.*, 2012). In the simulations, most of the gas is generated at a very low maturity: Vitrinite Reflectance Ro less than 0.6%. In this domain, it has been stated that the thermal C-C–bound breakage is unlikely to be significant without catalysis. Because microbial enzymes are the most efficient low-temperature catalysts known, this kinetic model could be described as a microbial enhanced thermal model.

PART 3: APPLICATION TO THE EASTERN MEDITERRANEAN "BIOGENIC PLAY"

The previous model has been applied successfully on different basins such as the Carupano Basin from the offshore Venezuela (Schneider *et al.*, 2012), Magdalena Delta (offshore Colombia) and the offshore Vietnam where direct observations of low-maturity gas were available. Furthermore, it has been applied in the offshore Lebanon in order to check the viability of a biogenic gas system (Dubille and Thomas, 2012; Dubille *et al.*, 2013; Schneider *et al.*, 2013).

The objective of this study was to assess, for the Ministry of Energy and Water of Lebanon, the hydrocarbon potential of the whole Offshore Lebanon, by evaluating petroleum systems at a regional scale (both thermogenic and biogenic), using the basin modeling methodology.

Geological context

The Offshore Lebanon comprises the continental margin (Mesozoic carbonate shelf and slope) and a large deep water area (*e.g.* Hawie *et al.*, 2013). They are part of the Levant sedimentary Basin bounded to the East by the Arabian Plate, to the south by Africa, to the west by Eratosthenes Continental Block and to the north by the Cyprus tectonic arc (subduction). This

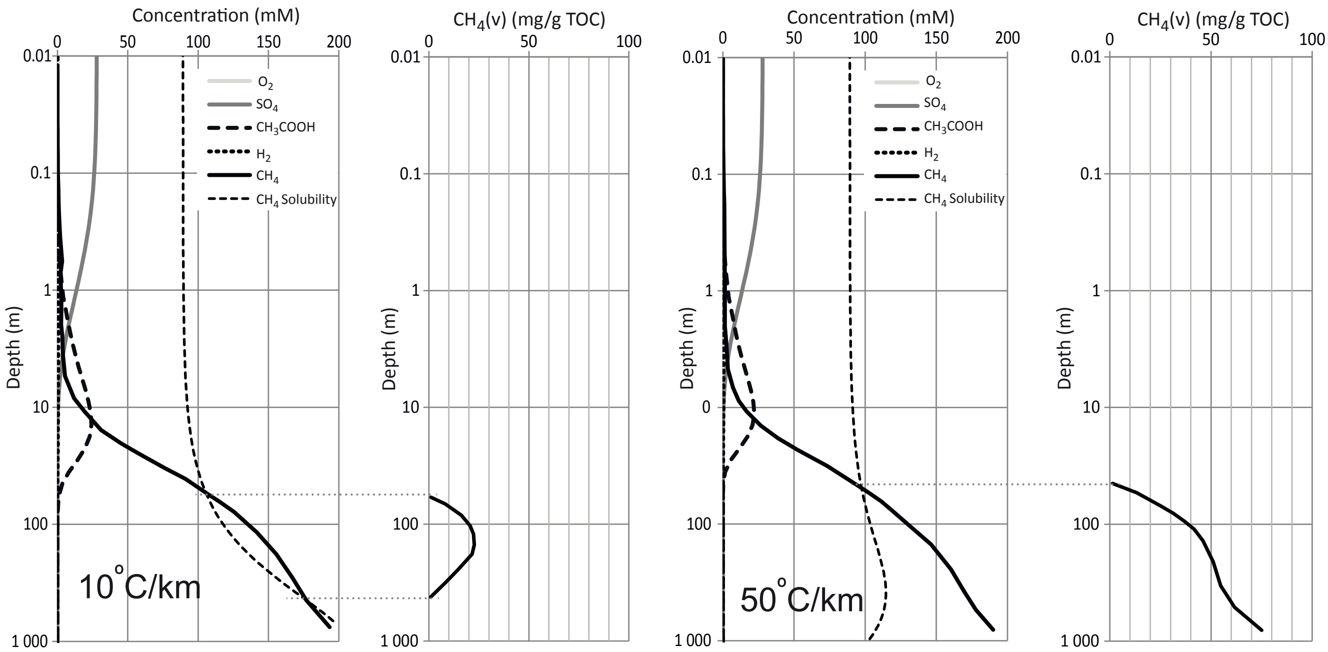

Figure 7. Left: Results of a simulation with a thermal gradient of 10ºC/km. Right: Result of a simulation with a thermal gradient of 50ºC/km. The comparison of the two simulations shows that one when the methane production increase when the thermal gradient increases because the methane solubility in water decreases when the temperature increases.

Basin resulted from the fragmentation of the Pangea by rifting and extension from Triassic to Middle Jurassic. While the margins are typical carbonate platforms with steep slopes, the 12 to 14km sedimentary infill of the basin comprise deep water pelagic and re-deposited clastic sediments at least since the Upper Jurassic and until Present time. It was affected by the Messinian Salinity Crisis with sub-aerial erosion of the margins and deposition of about 2000m thick evaporites in the deep basin, a major regional seal partly responsible for the under-compaction of the basin.

Offshore Lebanon is a frontier Basin with no drilled well in which hydrocarbon resources are not yet proven. However major gas discoveries have been made in the vicinity in Offshore Israel (Tamar, Leviathan) and Offshore Cyprus (Aphrodite) in sandy turbidites reservoirs of Lower Miocene age intercalated between Miocene and Oligocene shales. Moreover, the giant Zohr gas discovery in Egypt (close to Eratosthenes sea mount, announced in 2015) proved that shallow water carbonates of the margins connected to adjacent Miocene-Oligocene basinal shales can be gas reservoirs. When the study was carried out in 2011–2012 the biogenic nature of the gas was not yet confirmed and was still debated among the community (Dubille and Thomas, 2012; Dubille *et al.*, 2013; Schneider *et al.*, 2013).

The petroleum system study was preceded by an extensive geological and geophysical study. An integrated interpretation of regional 2D seismic surveys offshore Lebanon provided structural maps and an improvement of the geological knowledge. These data allowed the building of a geological model in 3 dimensions at the scale of the whole offshore Lebanon. The pressure field and the thermal field were calculated in this geological model through geological times, as well as the hydrocarbon generation / expulsion / migration. The thermal modeling included a modeling of the whole lithosphere. Thermogenic source rocks observed in surrounding basins were implemented and tested in the model.

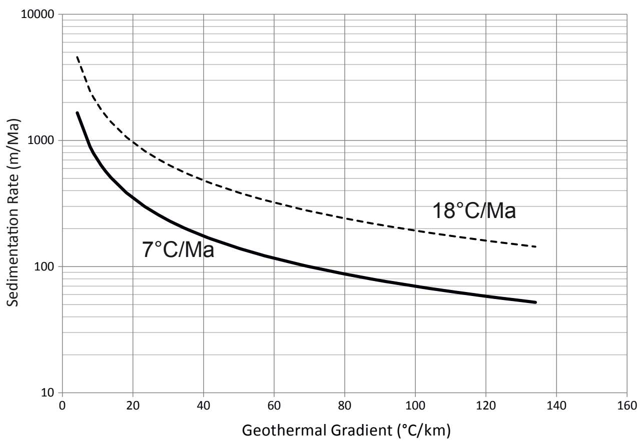

FIGURE 8. Modified Clayton's chart showing the equivalence in term of heating rate. The optimal geological condition for the biogenic gas generation and preservation in the geological system is comprised between both curves.

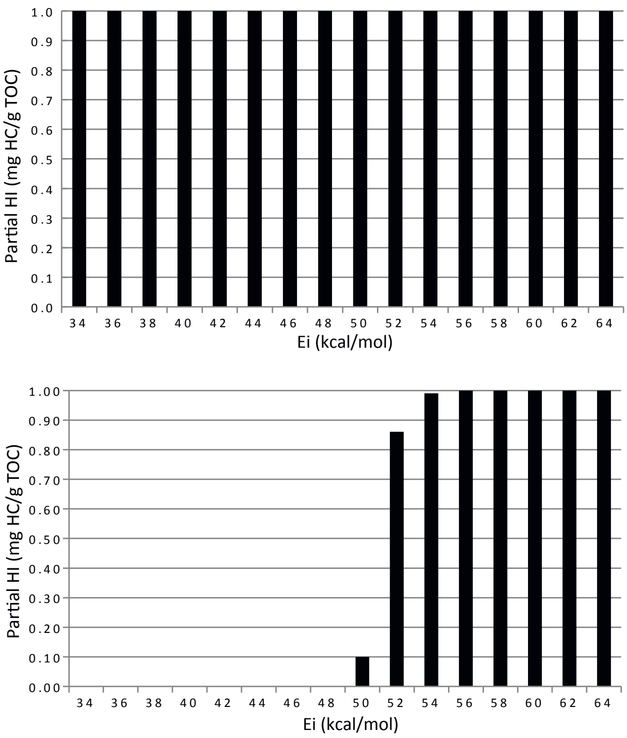

FIGURE 9. Artificial maturity experiment on a synthetic sample (A) with uniform distribution of partial potential and A= 3.1 $10^{15}s^{-1}$. At maturity equivalent to Ro= 0.6% (B) all the partial potentials have been totally consumed for activation energy below 50kcal/mol.

Modeling strategy

The analysis of the thermal gradient and the sedimentation rate allows defining the potential biogenic gas source rock. For example in the offshore Magdalena Delta, according to the geothermal gradient values in the studied area ranging from 14 to 20ºC/km, the optimum sedimentation rate for biogenic gas preservation is in the range 300 to 1500m/My.

In the case where the thermal gradient and the sedimentation rate present spatial variations, such as in offshore Lebanon, a methodology is proposed for identifying which parts of a layer could develop a biogenic gas generation and preservation potential. The thermal gradient and the sedimentation rate calculated at deposition time by TemisFlow3D® (in the uppermost layer of the model at a given time step) are multiplied for obtaining a "heating rate map at deposition time" (Figure 11). The generated maps give, for a given layer a first overview of the biogenic gas generation potential.

A map of the "Biogenic Gas Potential Index" is then edited using criteria on the Heating Rate map (heating rate values within the "Biogenic Window"), but also on the TOC and on the sedimentation rate. It is also considered that even if the heating rate exceeds 18ºC/My, a reduced biogenic gas potential may remain in the system. Moreover, the evolution of the heating rate of the rock after its deposition is checked too: if the pasteurization temperature is reached too quickly, then the potential is decreased.

Resulting maps of biogenic gas generation and preservation potential are interpreted in terms of remaining or effective Total Organic Carbon TOCe available for the biogenic gas system, considering the following assumptions:

i) When heating rate conditions are favorable for microbial generation and preservation ("highly probable" on the map Figure 12), the biogenic gas source rock is characterized with a full potential (TOC= TOCe).

ii) When the heating rate conditions are not favorable for the microbial generation and preservation ("no biogenic potential" on the map Figure 12), the concerned area is characterized with a null potential (TOC= 0%). Indeed, there is no effective biogenic potential.

iii) Intermediary Biogenic Gas Potential (0%<TOC<TOCe) are also defined when conditions are partially respected.

There was no geochemical data for calibrating the TOCe in Offshore Lebanon, so TOCe values have been

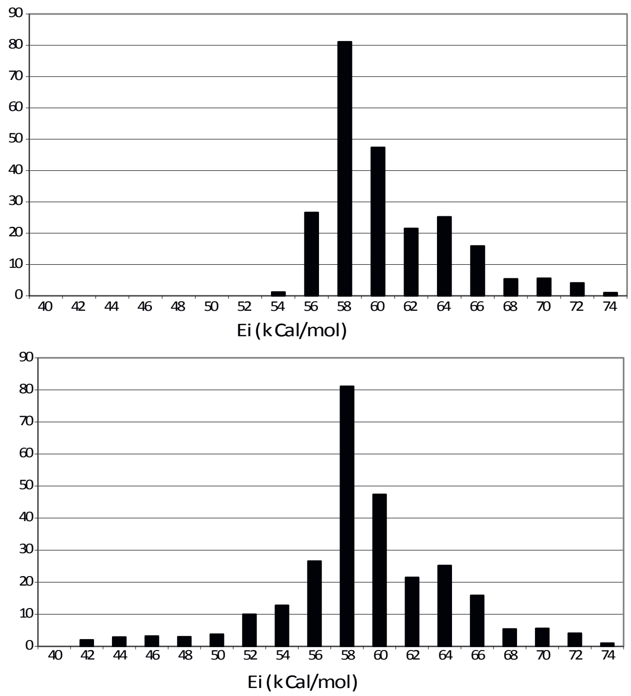

FIGURE 10. A) Original kinetic parameter for a Type III kerogen calibrated at Ro= 0.6%. B) Recalculated Type III kerogen at the beginning of the diagenesis window.

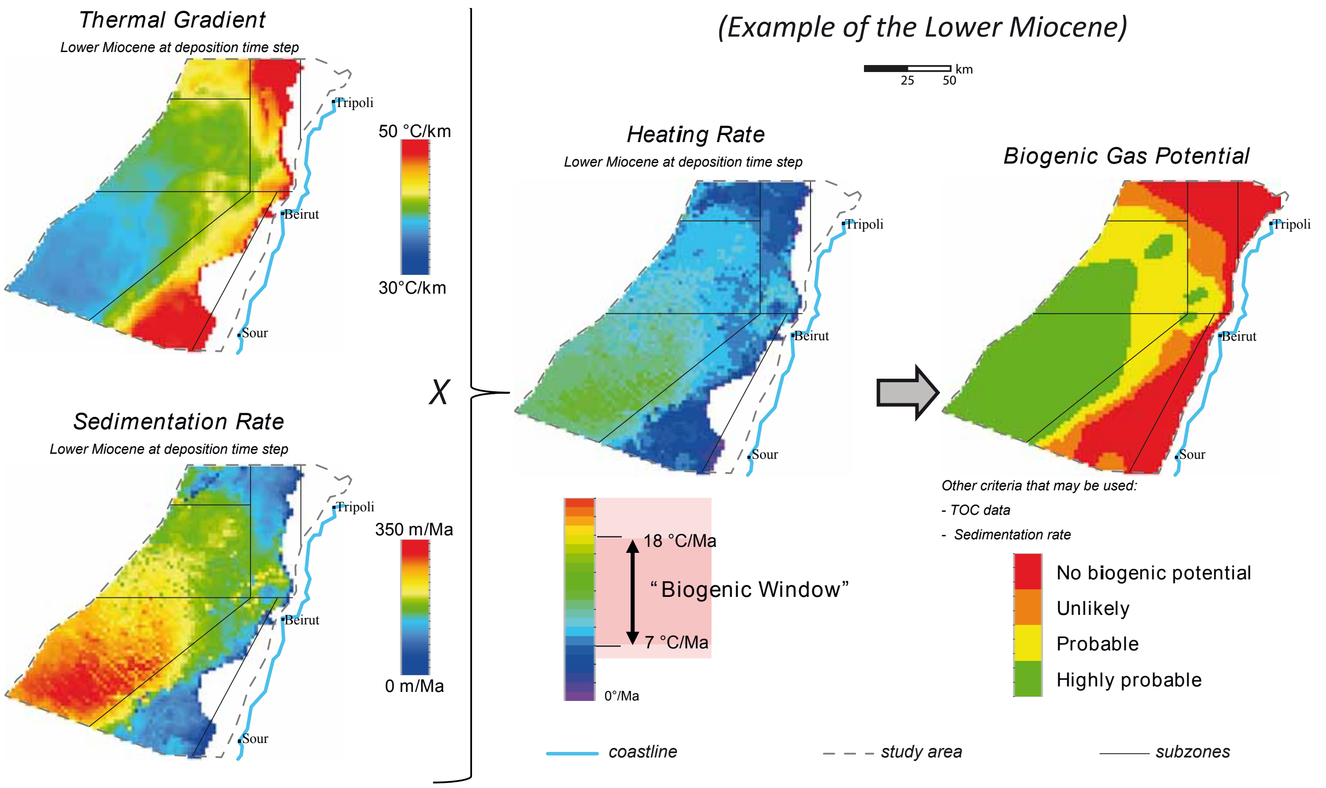

Figure 11. Illustration of the methodology that identify, for a given layer, the area that may produce microbial gas. The thermal gradient is calculated in the uppermost layer of the model, the average thermal gradient in the basin is much lower around 22ºC/km.

estimated from analogs. In the Carupano Basin, the "TOC_{SR} methodology" (see appendix of Schneider *et al.*, 2012) has been used in order to define continuous TOC profiles from sonic and resistivity wire logs in poorly compacted sediments. The method has been applied to all the wells that have a sonic and a resistivity logs. As a result, the average TOC content of the possible biogenic gas source rock is in the range 0.5 to 1.2% with a maximum averaged value of 2.5%.

In the case of offshore Lebanon, we assumed that the full potential of the biogenic gas source rock is set to TOCe= 1%. In intermediate zones the TOC equals 0.3% or 0.6%. The resulting methane generation potential varies between 0 and 1.25kg CH_4/m^3_{Rock}.

The screening of the different shaly layers in term of thermal gradient and sedimentation rate allowed defining seven levels with a possibility of generating microbial methane (Figure 12).

Results and discussion

The results of the TemisFlow® simulations show that the 2 shallow biogenic gas source rocks (Pliocene and Upper Miocene) did not expelled noticeable amount of microbial methane despite their initial potential (Figure 13). Main contributors to biogenic gas petroleum systems would be Middle-Lower Miocene and Lower Oligocene layers. The expulsion from this layer is also enhanced by the presence of closely interbedded reservoir sands and source shales in turbiditic sediments of the deep offshore Levant Basin (distal fan of the Nile Delta).

According to the model at present day, Lower Miocene and Oligocene sediments are beyond the pasteurization temperature in the deep basin: in these deep layers the biogenic methane generation ended after the Messinian Crisis (deposition of 2000m of salt). Large gas discoveries in offshore Israel are likely related to a biogenic system which is no longer active even if the gas expulsion from the source rocks continues up today at a lower rate.

The computed HC composition indicated that the gas, mostly biogenic, completely dominates the shallow plays from the Pliocene to the Oligocene. In particular, the Lower Miocene play which produces gas in Tamar and Leviathan is easily filled by biogenic gas. The oil/condensate content would increase in the Eocene, and overall in the Cretaceous–Jurassic. The gas content increases again in deep layers (mostly thermogenic gas), up to 100% in the Triassic play.

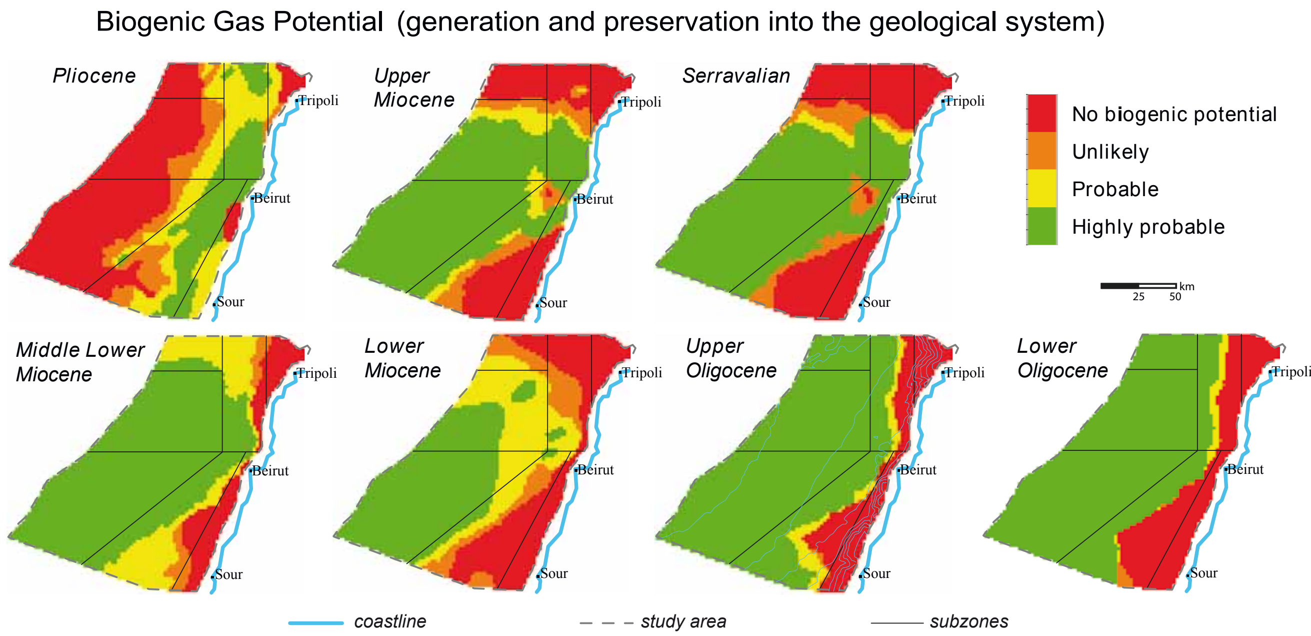

Figure 12. Definition of the possible biogenic generation zones for the 7 potential biogenic gas source rocks.

The results of the study indicate that there is petroleum potential in the offshore Lebanon. The most active systems would be:

i) The Oligo–Miocene biogenic gas source rock, with Upper Oligocene and Miocene clastic reservoirs. The main risk is the absence of deep-sea fans related to the Nile Delta or to other local contributors (mainly in the North along the Latakia Ridge). The dense Oligo–Miocene fault network in offshore Lebanon (Hawie *et al.*, 2013) may increase the vertical gas migration in shallower Middle and Upper Miocene reservoirs (below the Messinian Salt) but may also limit the size of drainage areas.

ii) The Upper Cretaceous thermogenic source rocks, with hypothetic Paleogene clastic reservoirs. The main risk is the absence of Upper Cretaceous SRs– which are well-known onshore Lebanon– in the deep offshore domain where the sedimentary context is not favorable (Bou Daher *et al.*, 2015). This system is largely disconnected to the biogenic plays in the basin, even if traces of heavier components may locally reach Neogene reservoirs (dense Oligo–Miocene fault network in offshore Lebanon rooted in a Paleogene detachment level).

iii) The Mesozoic thermogenic source rocks (Upper Cretaceous and Jurassic), with Mesozoic (in particular Jurassic) shallow water carbonate reservoirs or Lower Cretaceous clastic reservoirs. Deep Jurassic source rocks are poorly documented in the northern Levant Basin but described in its southern part (Gardosh *et al.*, 2006). In Lebanon their existence is possible on the Mesozoic carbonate platform (buried in the eastern half of the study area).

iv) The model also shows that the biogenic gas generated in Oligo–Miocene clastic sediments may locally migrate laterally within the Mesozoic carbonate platform. This possibility seems to be realistic as shown by the recent Zohr gas discovery (Offshore Egypt).

In the reference scenario the biogenic gas represents 40% of in place hydrocarbons at basin scale (and 60% of the gas), but only 20% of expelled hydrocarbons. Indeed the late expulsion (Mio–Pliocene) is favorable to methane accumulations in Neogene layers of the deep basin.

Many structures in Neogene reservoirs of the deep basin could be filled with biogenic methane, even without a thermogenic source rock contribution.

Coupling the Biogenic and the thermogenic model, the petroleum potential of the offshore Lebanon has been evaluated as a dry gas zone in its western part (dominant biogenic origin in the deep offshore basin), a reduced oil zone in its eastern part along the shore (limited petroleum potential), and an intermediate ribbon between the oil and the gas zones where both biogenic and thermogenic gas are expected, with the likely presence of condensates in Mesozoic reservoirs (Figure 14)

CONCLUDING REMARKS

In conclusions, the paper describes a model based on a substrate and microbes populations' evolution. In its first

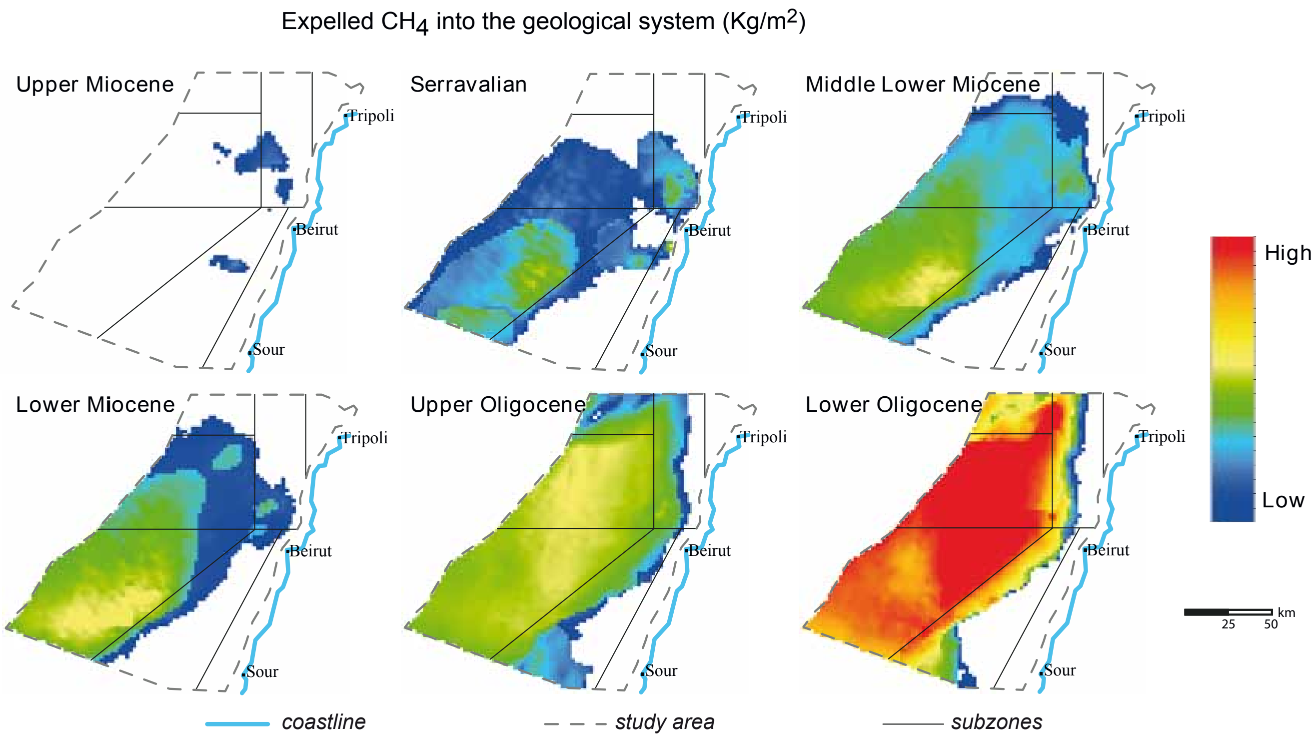

Figure 13. Cumulative expelled methane calculated by the model.

version, this model account satisfactory for seven groups of microbes which contribute to:

i) The aerobic oxidation of the OM
ii) The anaerobic sulfate reduction of the OM
iii) The anaerobic fermentation of the OM
iv) The anaerobic sulfate reduction of the acetate
v) The Acetotrophic Methanogenesis
vi) The Hydrogenotrophic Methanogenesis
vii) The Anaerobic sulfate reduction of methane

Other reactions will be added in future versions of the model. Some additional works are needed in order to calibrate or to constrain the numerous free parameters of the model.

The sensitivity analysis suggests that:

i) The preserved HOC is a function of the initial HOC, and that the preserved HOC increases as the sedimentation rate increases.

ii) The expulsion depth of methane increases as the sedimentation rate increases, and as the initial HOC decreases: The degazing of methane occurs closer to the surface in case of low sedimentation rate or high TOC.

iii) The production of methane in vapor phase increases as the thermal gradient increases because the methane solubility in water decreases as the temperature increases.

In order to be usable at basin scale in petroleum system models (TemisFlow®), this microscopic model is upscaled into a macroscopic model. It consists in:

i) A criterion that allows the definition of "efficient" biogenic gas source rocks in which the biogenic gas is not only generated but also preserved into the geological system. This criterion is based on the initial TOC, the sedimentation rate and the thermal gradient.

ii) A biogenic first order kinetics assuming that microbes are catalyst.

This approach has been tested and validated through some case studies carried out in Venezuela, Colombia and Vietnam. It has then been used in the offshore Lebanon in order to evaluate the active Neogene biogenic system in this area.

The results of the study indicate that there is petroleum potential in the offshore Lebanon. The most active systems would be:

i) The Oligo–Miocene biogenic gas source rock, with Upper Oligocene and Miocene clastic reservoirs.

ii) The Upper Cretaceous thermogenic source rocks, with hypothetic Paleogene clastic reservoirs and more probable Lower Cretaceous deep water clastic reservoirs.

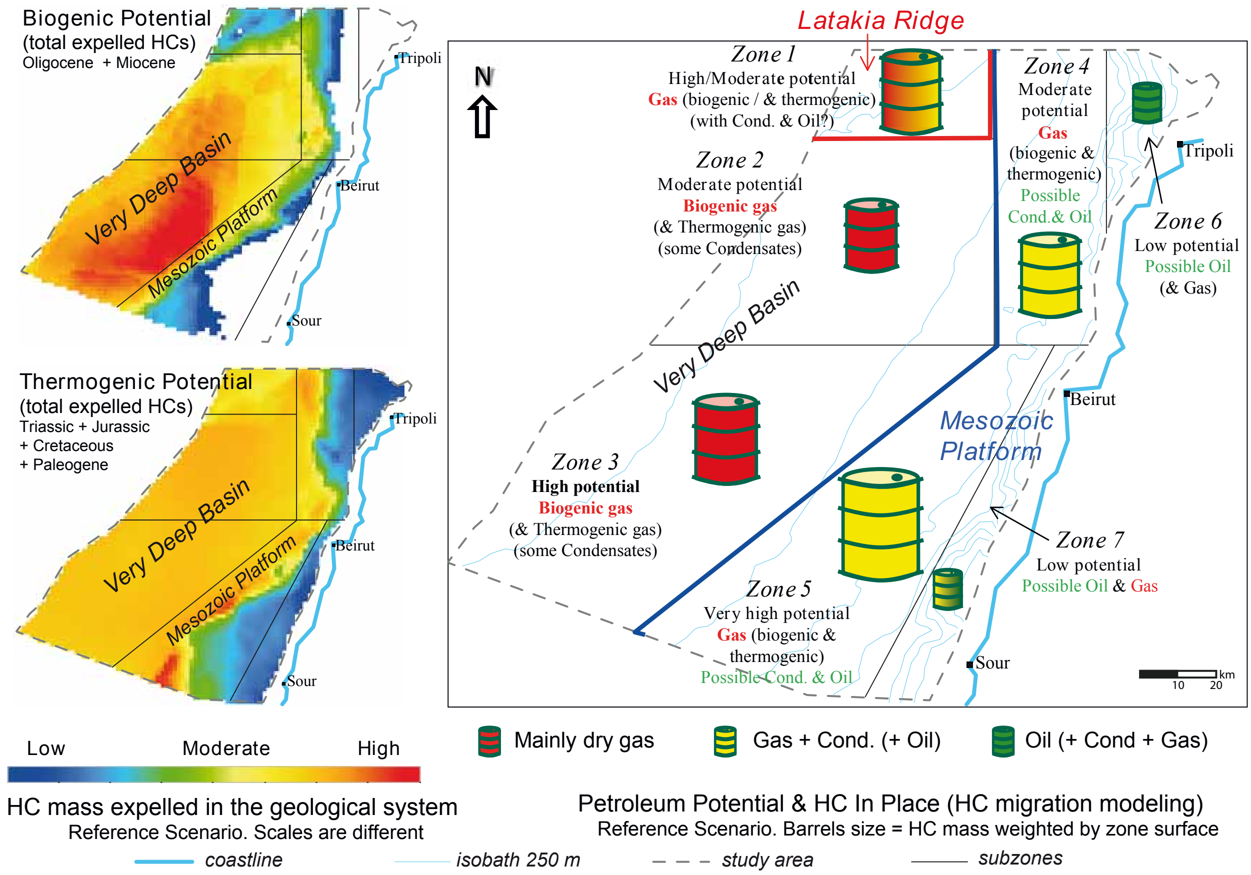

Figure 14. Synthesis of the results of the model in which the thermogenic generation model has been coupled with the biogenic generation model.

iii) The Mesozoic thermogenic source rocks (Upper Cretaceous and Jurassic), with Mesozoic (in particular Jurassic) shallow water carbonate reservoirs and Lower Cretaceous clastics.

In the reference scenario the biogenic gas represents 40% of in place hydrocarbons at basin scale, and 60% of the gas. TemisFlow® basin modeling results (2011–2012) have been validated by subsequent press releases (2013) that confirmed the existence in the Leviathan structure of a deep thermogenic system below Oligo–Miocene biogenic gas plays. A similar distribution of the hydrocarbon is expected in offshore Israel and offshore Lebanon. However the denser Oligo–Miocene fault network in offshore Lebanon could drive the biogenic gas and heavier hydrocarbons (wet gas/condensate) in shallower horizons of the deep basin, and would limit the gas migration eastward as well as the size of drainage areas.

The main uncertainty in the models is the initial TOC and HOC used for the definition of the biogenic gas source rocks. These values could be better constrained using data from close existing wells. Moreover the proposed workflow is under continual improvement: in the near future, the next steps are the integration of methane dissolution and adsorption processes in the petroleum system model. The objective is to better understand the early preservation of the dissolved methane in the source rock, its expulsion and its migration in dissolved form or in vapor phase at basin scale through geological times (achieved in recent study cases). Therefore the impact of the Messinian crisis on the methane degassing will be better quantified in the offshore Lebanon study case. Furthermore, research works propose the existence of a "labilizable" organic matter which undergone a very early thermogenic transformation into "labile" organic matter (Pujol *et al.*, 2016), bringing an additional source of carbon to methanogen bacteria through geological time.

Recent works seem to demonstrate that the same deep biosphere is responsible for early gas generation and biodegradation of thermogenic hydrocarbons. For example Milkov (2011) proposes that large gas pools in Western Siberia are sourced by biodegradation processes. Furthermore, the exploration for unconventional gas demonstrated that late biogenic gas can be generated from old source rocks. The existence of biogenic coalbed methane (Rice, 2000) also shows that methanogenesis can be efficient on a large range of substrates. Further efforts should be done toward a better modeling of the effects of the deep biosphere on the petroleum systems.

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