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# 1 Quantification of natural microbial methane from 2 generation to emission in the offshore Aquitaine: A basin 3 modelling approach

4 Martina Torelli<sup>1</sup>, Isabelle Kowalewski<sup>1</sup>, Veronique Gervais<sup>1</sup>, Johannes Wendebourg<sup>2</sup>, Stéphanie  
5 Dupré<sup>3</sup>, Sylvie Wolf<sup>1</sup>, Claude Gout<sup>4</sup>, Eric Deville<sup>1</sup>

6 <sup>1</sup>IFP Energies Nouvelles, 92852 Rueil-Malmaison Cedex, France

7 <sup>2</sup>Total Exploration Americas, Houston, TX, 77027, USA

8 <sup>3</sup>Ifremer, Géosciences Marines, 29280 Plouzané Cedex, France

9 <sup>4</sup>Total, Exploration and Production, Pau Cedex, France

## 10 11 ABSTRACT

12 Marine sediments near continental margins contain sedimentary organic matter (SOM) which is  
13 subject to the metabolic activity of micro-organisms during early diagenesis resulting in production of  
14 biogenic methane. This process occurs at microscopic scale and anaerobic conditions. Here, we apply  
15 a new numerical approach to simulate biogenic methane production offshore Aquitaine (Bay of  
16 Biscay) where gas seeps have been recently observed as the result of microbial activity. This new  
17 approach accounts for: (1) degradation of a labile-SOM fraction to methane, (2) first order kinetics of  
18 the thermal degradation of a thermo-labile-SOM fraction into labile fraction at greater burial and (3)  
19 decrease of SOM reactivity with time. First, the organic matter is characterized through pyrolysis  
20 using Rock-Eval performed on cuttings collected from two wells located within the methane seepage  
21 area. The microbial system is fed from a type III continental-derived SOM which is immature (average  
22  $T_{max} < 425^{\circ}\text{C}$ ). The basin model is built and calibrated on seismic and well data. It accounts for the  
23 consumption of methane required to precipitate methane-derived authigenic carbonates which are  
24 found widely distributed on the seafloor as the result of the anaerobic oxidation of methane during  
25 upward migration. A sensitivity analysis is performed on the main model input parameters to quantify  
26 their impact on the biogenic gas production and expulsion/migration processes. Results led to a  
27 reference scenario for microbial gas production in offshore Aquitaine. With this model the generated  
28 methane is predominantly dissolved in water and transported by advective processes. Migration is  
29 mainly vertical from the source rock layers to the seafloor and controlled by sediment porosity and  
30 strata geometry. Modelling can reproduce natural processes such as gas migration at emission points  
31 (gas seeps) which have been previously mapped in the offshore Aquitaine Basin. Our results suggest  
32 that the biogenic methane is sourced by a present-day active system with a mean flow rate of 27 Mg/y  
33 which is relatively lower than flux modelled during the early Pleistocene reaching up to 41 Mg/y.  
34 Calculated total methane lost to the seafloor along the Aquitaine Shelf is in accordance with methane  
35 flow rate estimated from in situ measurements and acoustic signatures of bubbling sites, and ranges  
36 between 0.87 Tcf/My and 1.48 Tcf/My. Here we propose a new workflow to assess and predict  
37 biogenic gas occurrences in offshore environment at the basin scale where gas is sourced by recent

38 continental-derived organic matter. This new approach can help to better assess the total biogenic  
39 methane budget emitted naturally in the shelf area of oceans that may reach the atmosphere with a  
40 negative impact on climate and environment.

41 **Key words: Biogenic Methane, Basin Modelling, Methane-Derived Authigenic Carbonates**  
42 **(MDAC), Anaerobic Oxidation of Methane (AOM), Sensitivity Analysis, Sedimentary Organic**  
43 **Matter (SOM), Aquitaine Shelf**

## 44 **1. INTRODUCTION**

45 Over the last few decades, natural gas has received increasing attention concerning its application as a  
46 major and cleaner energy source compared with coal and liquid fossil fuel (Rice and Claypool 1981;  
47 Rice 1992, 1993; Whiticar 1994; Kvenvolden 1993; Katz 2011). It is estimated that the annual  
48 methane emission from geo-sources only (onshore mud-volcanoes, onshore gas-oil seep, submarine  
49 seepage, micro-seepage, geothermal-volcanic manifestations) directly in the atmosphere yields  
50 between 27 – 63 Megatons (Etiopie and Schwietzke, 2019), with a negative impact on the global  
51 climate (IPCC, 2013; Khalil et al. 1993; Judd et al. 2002; Dickens 2004). Even though several  
52 estimates have been published over the past years (Hornafius et al. 1999; Judd et al. 2002; Judd et al.  
53 2004; Kvenvolden et al. 2001; Etiopie et al. 2008; Etiopie and Klusman 2010) our understanding of the  
54 methane budget is still uncertain (Etiopie and Klusman 2002; Sauniois et al. 2016; Schwietzke et al.  
55 2016; Etiopie and Schwietzke 2019) especially concerning the potential of natural methane sources  
56 from sedimentary basins resulting from microbial activity and/or thermal cracking of buried  
57 sedimentary organic matter (Klusman et al. 2000; Etiopie and Klusman 2002). It is well accepted that  
58 fluid emanations through the ocean floor are ongoing processes represented by characteristic  
59 geological features that are widely distributed along near-shore, continental slope and in deep ocean.  
60 They include shallow gas accumulations, pockmarks, seeps, mud-volcanoes, authigenic carbonate  
61 precipitations and gas hydrates (Jensen 1992; Römer et al. 2012; Skarke et al. 2014; Dupré et al. 2007;  
62 Pierre et al. 2017; Hovland et al. 2002; Judd et al. 2002).

63 Methane generation is the result of Sedimentary Organic Matter (SOM) degradation which takes place  
64 at different diagenesis stages (Whiticar et al. 1986; Floodgate and Judd 1992; Whiticar 1999; Schulz  
65 and Zabel 2006). In addition to the degradation process of SOM, methane production is controlled by  
66 other factors such as temperature, primary productivity, sedimentation rate (Clayton 1992; Judd et al.  
67 2002) and the microorganisms mediating the reaction (Boetius et al. 2000). Biogenic systems can be  
68 sourced by poorly-OM layers (TOC < 0.5%) (Clayton 1992). This process is usually observed in  
69 deltas where large amounts of sediment are deposited in a short time, containing low continental-OM  
70 dispersed in sediments such as the Amazon Delta (TOC  $\square$  0.8%) (Arning et al. 2013) or in the

71 Japanese Pleistocene turbiditic sequences of the eastern Nankai Trough (TOC  $\approx$  0.5%) (Fujii et al.  
72 2016). Methanogenesis in low organic matter sediments is also observed in the Great Australian Bight  
73 (TOC < 0.4%) (Mitterer 2010) and in the Woodlark Basin (TOC < 0.4%) (Wellsbury et al. 2002).  
74 Therefore, a better understanding of the microbial gas generation process at a large scale is necessary  
75 to identify the distribution of methane in the subsurface. In addition, quantifications of natural  
76 methane sources and sinks, both at the present day and in the geological past, are of interest to the  
77 scientific community working on present and future global climate change (Regnier et al. 2011;  
78 Saunois et al. 2016).

79 Numerical modelling is a way to study the interactions of the various geological processes leading to  
80 biogenic gas generation, accumulation and migration as these interactions cannot be reproduced in the  
81 laboratory given the large spatial dimensions and the slow natural reaction and migration rates.  
82 Modelling can be used to critically evaluate and discuss the significance and the role of the main  
83 parameters that lead to biogenic gas accumulations. However, it is a challenge to integrate the  
84 microscopic processes of methane production at the basin scale. In this paper, we present a  
85 quantitative model of the total methane volume generated from microbial activity and emitted offshore  
86 Aquitaine (Bay of Biscay, SW France) that is compared with an estimation of emitted methane based  
87 on both in situ measurements and acoustic records of a few thousand bubbling sites (Dupré et al. 2020)  
88 (Fig. 1). Our approach consists in simulating the biogenic gas generation and migration with a 3D  
89 basin model of the study area using a recent numerical implementation for microbial processes  
90 modified after Pujol et al. (2016).

91 For biogenic gas generation, our model considers that the initial Total Organic Carbon (TOC) can be  
92 partitioned into three different fractions (Fig. 2). A labile fraction called TOClab is composed by the  
93 OM that is sensitive to biodegradation from the beginning of deposition (Wallman et al. 2006). A  
94 thermo-labile fraction called TOCzlab is composed by the OM that is less reactive and therefore can  
95 be preserved in the mineral matrix (Burdige et al. 2007, 2011). The third bio-refractory fraction called  
96 TOCbio-ref represents the part of the OM which is later converted to hydrocarbons by thermal  
97 cracking when the temperature increases above 80°C (Fig. 2). In our model, this temperature  
98 corresponds also to the pasteurization temperature of the micro-organisms (Rice and Claypool 1981;  
99 Clayton 1992). Average percentage of TOCbio-reactive for a typical Type II marine OM are: TOClab  
100 = 30-40% (Burdige 2007; Wallmann et al. 2006) and TOCzlab = 8-15% (Burdige 2011).  
101 Unfortunately, such fractions have not been described for continent-derived terrestrial type III-OM  
102 such as found in the Offshore Aquitaine (Michel 2017). It is well known that terrestrial organic matter  
103 is mainly composed by higher plants characterized by lower hydrogen and higher oxygenated  
104 functional groups contents than marine OM (Burdige 2011; Kamga 2016). When entering in the  
105 marine environment, the terrestrial OM is probably already highly altered (Zonneveld et al., 2010).  
106 Then, the degradation of OM is followed by an evolution of its molecular composition and its

107 association with the mineral matrix, which tends towards an increasingly refractory nature. As a result,  
108 type-III OM dispersed in sediments is less reactive and more thermally-resistant than type II organic  
109 matter specially at low temperature (Cowie et al. 1992; Burdige 2007, Kamga 2016). Here, we  
110 described the OM based on data available in the literature concerning the geochemical characterization  
111 and degradation rate of recent continental-OM (Cowie et al. 1992; Martens and Canuel 1996; Hedges  
112 and Oades 1997; Burdige 2007, 2011). However, the fraction of the terrestrial organic carbon  
113 preserved in marine sediments is still poorly constrained.

114 The offshore Aquitaine is a unique case study as (1) methane is purely of microbial origin and not  
115 related to a thermogenic petroleum system or gas hydrates, (2) there is evidence of persisting methane  
116 circulation over time in the form of Methane-Derived Authigenic Carbonates (MDAC) pavements and  
117 (3) the quantity of released methane along the shelf at the present day is rather widespread and  
118 important (144 Mg/y) (Dupré et al. 2014; 2020; Pierre et al. 2017; Ruffine et al. 2017). In this study,  
119 we build a 3D sedimentary model of the offshore Aquitaine that includes a lithospheric model  
120 allowing to account for the thermal history of the basin. The model is calibrated with eleven wells that  
121 are regionally distributed over the study area (Fig. 3). It also takes into account the MDAC deposits.  
122 However, as mentioned above, some parameters related to biogenic gas generation are still uncertain.  
123 Thus, we performed a sensitivity analysis to study the impact of these parameters on biogenic gas  
124 generation. More precisely, we sampled the parameter space and simulated gas generation and  
125 migration for the corresponding set of models to estimate sensitivity indices. Finally, we used the  
126 available gas flow rate data to identify a realistic scenario among the sample. The biogenic CH<sub>4</sub> budget  
127 for the offshore Aquitaine was calculated for this model, taking the presence of MDAC into account,  
128 and compared with locations and quantities of observed natural emissions. According to our results, a  
129 gas system originating from only microbial activity can be active over millions of years and can  
130 generate important volumes of methane which may either be trapped in the sediments or directly  
131 escape to the seafloor, depending on the specific geological settings.

132 The paper outline is as follows. First, the geological setting of the case study is introduced, followed  
133 by a description of the data set used to build the 3D basin model. The workflow used to quantify the  
134 generated biogenic gas is described in section 4. It encompasses the definition of the 3D sedimentary  
135 model, the modelling of the processes of biogenic gas production and migration, and the sensitivity  
136 analysis on the uncertain parameters. The application of this workflow to the Aquitaine Basin is  
137 described in section 5, followed by some discussions of the results in section 6.

## 138 2. GEOLOGICAL SETTING

### 139 *Geodynamic Evolution of the Bay of Biscay*

140 The study area is located in the Bay of Biscay which is bordered by the Armorican Shelf in the North  
141 and by the narrow and shallow Basque plateau in the South (Ferrer et al. 2008; Roca et al. 2011;  
142 Tugend et al. 2015). The opening of the Bay of Biscay was influenced by the structuration of the  
143 Variscan orogeny and is the result of different extensional and compressional cycles (Tugend et al.  
144 2014), and notably two rift systems (Ferrer et al. 2008; Tugend et al. 2014): a first North Atlantic  
145 rifting phase at the beginning of the Triassic, followed by a second rifting phase during late Triassic to  
146 early Jurassic which induced crustal thinning (Boillot et al. 1979) and the formation of intracontinental  
147 basins such as the Aquitaine Basin. During the Santonian, the opening of the Atlantic Margin induced  
148 a compressional deformation in the southern Bay of Biscay and a weak compressive reactivation in the  
149 northern area (Thinon et al. 2001; Tugend et al. 2014). This compressional movement led to the  
150 inversion and reactivation of extensional structures which initiated the Pyrenean orogenesis. The  
151 major compressional phase was reached during the Eocene and lasted until the end of the Oligocene. It  
152 resulted in the accretion of the Pyrenean chain and the formation of the foreland Aquitaine Basin  
153 (Tugend et al. 2014). The main target area of our study is the Aquitaine Shelf (Fig. 1) which is part of  
154 the offshore Parentis Basin and also represents the main hydrocarbon province of France (Biteau et al.  
155 2006). It is filled-up with 15 km of sedimentary cover over a relatively thin crust (Biteau et al. 2006;  
156 Bois et al. 1997; Ferrer et al. 2008).

### 157 *Stratigraphic Framework*

158 This section presents an overview of the Aquitaine Basin stratigraphy. For a more detailed  
159 stratigraphic description, readers can refer to Biteau et al. (2006).

160 The sedimentary column is composed at the bottom of a thick evaporitic sequence (anhydrite and salt)  
161 deposited in the Triassic during a period of high subsidence.

162 During the Jurassic, deposition was mainly characterized by the development of a westward carbonate  
163 shelf: limestones and shale during the Lias, limestones and dolomites during the Dogger. In Oxfordian  
164 time, extensional tectonics accelerated which led to the differentiation of the Bay of Biscay into  
165 various structural units such as the Parentis Basin where limestone deposition continued, with locally  
166 condensed sections until the Kimmeridgian (Biteau et al. 2006). During the late Jurassic the  
167 depositional environment became increasingly marine followed by the deposition of the “Mano  
168 Dolomite”.

169 The Early Cretaceous corresponds to the deposition of undifferentiated marly sediments representative  
170 of a shelf environment. During the Aptian, sediments in the Parentis area were characterized by  
171 carbonate deposits marking a transgressive period. During the Albian, pelagic shales were deposited,

172 including locally clastic turbidites. The Pyrenean compression started during the Upper Cretaceous  
173 when the Parentis Basin continued to record a thick sequence of shaly limestones and clays (Biteau et  
174 al. 2006).

175 The beginning of the Cenozoic was a period of decreasing sedimentation rates within an open marine  
176 context where the continental influence was marked by the presence of numerous marls. During the  
177 Oligocene a carbonate shelf developed westwards filled with marly deposits. From the Miocene until  
178 today, the area was covered by continental sediments.

### 179 ***Fluid escape features in the Aquitaine Basin***

180 An active fluid system along the Aquitaine Shelf was recently discovered based on previously  
181 acquired data collected during recurrent marine expeditions conducted by Ifremer (Pegase98,  
182 <https://doi.org/10.17600/98040070> and Pelgas2000 to 2011, <https://doi.org/10.18142/18>). Several echo  
183 soundings were recorded in the water column caused by gas bubbles located at 140-220 m water depth  
184 (Dupré et al. 2014). This fluid system has been further assessed during the GAZCOGNE1 (Loubrieu  
185 2013) and GAZCOGNE2 surveys (Dupré 2013). It extends over 375 km<sup>2</sup> along the Aquitaine Shelf,  
186 with 2612 bubbling sites (Dupré et al. 2020) (Fig. 1).

187 Molecular and isotopic analysis on gases ( $\delta D$  and  $\delta^{13}C$ ) revealed that these fluids are composed of  
188 almost pure biogenic methane (> 99.94% mol of the gases) generated from CO<sub>2</sub> reduction (Ruffine et  
189 al. 2017) without any link to the thermogenic sources from the Parentis Basin. Associated with these  
190 gas escapes, authigenic carbonate pavements are widely developed above and below the sub-seafloor  
191 over 375 km<sup>2</sup> (Pierre et al. 2017; Dupré et al. 2020). The bubbling sites, as well as the authigenic  
192 carbonates, are located east of the continental shelf break (Fig. 1) and no such activities were observed  
193 along the slope or inside the erosional canyon where the uppermost Pleistocene layers were removed  
194 (Michel et al. 2017; Dupré et al. 2020). Plio-Pleistocene and Holocene deposits are potential  
195 candidates for the source layers from which the microbial methane is generated (Dupré et al. 2020) as  
196 they record high sediment and organic matter supply (Cremer 1983).

197 Several scenarios for the source rock layers were investigated by Michel (2017). Based on regional  
198 horizon geometry from seismic data, geochemical evidence from Rock-Eval analysis and potential  
199 migration pathways, the source rocks for microbial methane are most likely located within the Upper  
200 Pleistocene progradational units (Michel 2017). However, based on the regional thermal gradient  
201 (Biteau et al. 2006) and temperature ranges for microbial activity (Katz 2011), it cannot be excluded  
202 that deeper source rocks may also contribute to the microbial gas generation (Dupré et al. 2020).

203 The isotopic signature of the carbonate cements demonstrates that these sedimentary features are the  
204 result of Anaerobic Oxidation of Methane (AOM) (Pierre et al. 2017). The precipitation of the  
205 methane-derived authigenic carbonates takes place within the Sulphate-Methane Transition Zone

206 (SMTZ) which corresponds to an oxic-anoxic boundary located in most cases below the seafloor at  
207 variable depth (Boetius et al. 2000).

208 These shallow-water seeps in the Aquitaine Basin are very different from classical deep-sea cold water  
209 seeps. As proposed by Pierre et al. (2017a) this system could be compared with seeps found along the  
210 northern U.S. Atlantic Margin (Pierre et al., 2017b) where methane emission sites have been  
211 discovered at 50-1700 m water depth as the result of freshwater discharge to the seafloor more than  
212 100 km away from the coast (Cohen et al. 2010; Skarke et al. 2014). Indeed, based on the oxygen  
213 isotopic signature of bulk carbonate and aragonite cements, MDAC from the Aquitaine Shelf  
214 precipitated from a mixture of seawater and freshwater as the result of submarine groundwater  
215 discharge at the seafloor (Pierre et al. 2017). This fluid system is highly dynamic. Therefore, it is  
216 easily influenced by the depth variations of the AOM and SMTZ, and possibly by the amount of  
217 groundwater discharge at the seafloor and along the slope where the erosion within canyons partially  
218 removed the uppermost sources of the biogenic methane.

219 This process linked to the precipitation of MDAC could be the reason why the location and migration  
220 of the methane seeps occur east of the shelf break. Indeed, emission sites are mainly located along a  
221 narrow band oriented N-S parallel to the Aquitaine Shelf with highly variable amount of emitted gas  
222 or MDAC deposits (Dupré et al. 2020). The fluid activity is more intense in the southern part of the  
223 basin compared with the northern part and the same differences are observed for the MDAC deposits  
224 which are widely distributed in the southern part and more localized in the northern area (Dupré et al.  
225 2020). Note that both thickness and initial age of the MDAC are still unknown. Based on Dupré et al.  
226 (2014; 2020) gas migration pathways are mainly controlled by sedimentary processes (indicated by  
227 precipitation of MDAC) rather than by tectonic activity (faults). As MDAC pavements can have a  
228 major control on the gas migration and they represent a major sink for methane, we accounted for the  
229 AOM in our model. The study area is located in the northern part of the Aquitaine Basin where the  
230 flow rate of methane emitted into the water column is estimated to be around 35 Mg/y (Dupré et al.  
231 2020) (Fig. 1b).

### 232 **3. DATA SET**

#### 233 *Source rock samples*

234 The geochemical characterization of the organic matter was done through Rock-Eval analysis  
235 (Espitalié et al. 1977; Espitalié et al. 1985; Lafargue et al. 1998). Based on previous studies (Michel  
236 2017; Dupré et al. 2020) and on the regional geothermal gradient (Biteau et al. 2006), it is accepted  
237 that the main target zone for biogenic gas production in our system is located at shallow depths in the  
238 Plio-Pleistocene progradational systems. However, deeper source rocks may take part in the



239 generation of microbial methane (Dupré et al. 2020). Thus, we collected samples between 595-1530 m  
240 bsf in the Plio-Pleistocene to upper Miocene sediments (Table S1). Exploration wells usually target  
241 reservoirs and not source rocks that are deeper so that samples from cores are rarely available at these  
242 depths. Nevertheless, 20 cuttings were collected from two exploration wells (Pelican-1, Pingouin-1)  
243 located at the external shelf area (Fig. 3). Cuttings are broken pieces of rocks derived from drilling  
244 processes. They are used to make a record of the investigated rock with a depth uncertainty of around  
245  $\pm 15$  m related to recovery operation. Considering that the minimum thickness of the source rock layers  
246 defined in our model is greater than 15 m, this uncertainty was assumed acceptable for our case study.  
247 All samples were washed, desalted and prepared in accordance with the procedure applied at IFPEN  
248 (Lafargue et al. 1998; Behar et al. 2001).

### 249 *Maps and well data*

250 Interpreted seismic horizons from the top basement to Cretaceous were taken from the OROGEN  
251 project (funded by Total, BRGM, CNRS & INSU), and from base Miocene to seabed from Ortiz et al.  
252 (2020), and they were used to construct a 3D model of the Bay of Biscay (Table 1). The interpretation  
253 of the three main units composing the Plio-Pleistocene progradational system are given in Michel  
254 (2017) (U1, U2 and U3, Table 1). Eleven exploration wells were drilled by Elf Aquitaine in the area of  
255 interest during the 60s, 70s and 80s. They are mainly located along the coast and along the shelf-break  
256 area as shown in Fig. 3. Measurements performed at these wells provide data used to calibrate the  
257 basin model as described in the next sections: facies logs, uncorrected Bottom Hole Temperatures  
258 (BHT) for 7 wells (see Fig. 7), vitrinite reflectance for 6 wells (Fig. 8) and pressure at two wells (Fig.  
259 S1).

260 Correction of BHT measurements can be more than 10% above the actual measure (Deming 1989).  
261 Because no information about the mud circulation time was found in the composite logs, it was  
262 decided to correct these measurements by adding 10% of the measured value and to consider an  
263 uncertainty of  $\pm 10\%$ .

264 Vitrinite reflectance data yield information about the maximum temperature experienced by the  
265 sediments (Jones and Edison 1979; Oberlin, 1980; Carr 2000). The measurements however were  
266 reported without any description of the sample type (e.g. dispersed organic matter, coal, extracted  
267 kerogen), therefore these measurements remain questionable. Pressure measurements indicate  
268 hydrostatic gradients which have been used to determine the average water salinity in the offshore  
269 Aquitaine Basin.

## 270 4. METHODS

### 271 *Rock Eval analysis to determine biogenic gas generation potential*

272 The Rock-Eval technique is widely used in academia and petroleum industry to determine the  
273 hydrocarbon potential, type and maturity of source rocks (Espitalié et al. 1977; Espitalié et al. 1985;  
274 Lafargue et al. 1998; Behar et al. 2001). This type of analysis is applied either on bulk rock samples  
275 (Espitalié et al. 1977) or on isolated kerogens or coals (Behar et al. 2001). The Rock-Eval technique  
276 consists in a thermal analysis of the sample through two analytical steps with specific temperature  
277 programs: a pyrolysis under inert atmosphere (N<sub>2</sub>) followed by a combustion of the residual sample  
278 under an oxidative atmosphere (air). The hydrocarbons are detected using a Flame Ionization Detector.  
279 The CO<sub>2</sub> and CO released by the pyrolysis and oxidation phases are continuously swept towards an  
280 infrared detector (Espitalié et al. 1985). A small amount of crushed source rock (about 70 mg) or  
281 isolated kerogen (5 to 30 mg) is usually exposed in the pyrolysis oven to a temperature of 300 °C for 3  
282 minutes before applying a heating rate at 25°C/min up to 650 or 800°C respectively. But since our  
283 samples are recent sediments containing immature organic matter, we applied a lower isotherm and the  
284 samples were heated at an initial temperature of 200°C as proposed in Baudin et al. (2015). During the  
285 pyrolysis cycle, three peaks are detected. The S1 peak obtained during the pyrolysis isotherm  
286 determines the amount of free hydrocarbons in the samples (mg HC/g of rock). The S2 peak obtained  
287 during the pyrolysis heating rate corresponds to the hydrocarbons released by thermal cracking (mg  
288 HC/g of rock). This S2 peak represents the remaining hydrocarbon potential of a source rock. The S3  
289 peaks partly correspond to the amount of CO and CO<sub>2</sub> released during thermal cracking (mg CO or  
290 CO<sub>2</sub>/g of rock). The main parameters calculated from Rock-Eval data are: Total Organic Carbon  
291 (TOC%) representing the total organic carbon content, Hydrogen Index (HI) (mg HC/g TOC) and  
292 Oxygen Index (OI) (mg CO<sub>2</sub>/g TOC). These parameters are used to determine the type (e.g. lacustrine,  
293 marine or continental) and the maturity of organic matter. Another parameter is also used as a proxy  
294 for the maturity of a source rock: Tmax (°C) that corresponds to the temperature measured at the peak  
295 of S2.

### 296 *Basin modelling*

#### 297 *Sedimentary model*

298 The static model of the Aquitaine Basin was built based on present-day topography (Ortiz et al. 2020)  
299 and 13 subsurface horizons that were derived from seismic interpretations (Table 1) (Michel 2017;  
300 Ortiz et al. 2020; M. Roger, personal com.). The surface of the model area is around 2800 km<sup>2</sup> (Fig. 3),  
301 divided horizontally into grid blocks of 1x1 km<sup>2</sup>. The model also includes the methane-derived  
302 authigenic carbonates distribution at the sub-seafloor (Dupré et al. 2020). The eleven exploration wells  
303 were used to cross-check the depth maps (Fig. 3). Finally, each isopach was associated with a

304 lithofacies map (Fig. 3). The facies distribution was obtained by well log correlation, with an  
305 additional uppermost MDAC layer for wells located within the sub-seafloor MDAC area (i.e. Pelican-  
306 1 and Fregate-1) (Figs 3, 7 and 8). The paleo-bathymetry for each horizon was defined in accordance  
307 with literature (Desegaulx and Brunet 1990; Brunet 1994). In order to more accurately model the  
308 processes of biogenic gas generation, the vertical resolution was increased in the main zone of  
309 biogenic gas production. Thus, the shallower strata from the Miocene to the Plio-Pleistocene layers  
310 were subdivided into several sub-layers (Table 1). The Miocene layer, which presents an average  
311 thickness of 600 m, was subdivided into six 100 m-thick sub-layers. The Plio-Pleistocene units U2 and  
312 U3 were also refined. The U2 unit was subdivided into seven sub-layers with an average thickness of  
313 60 m. The U3 unit was subdivided into eight sub-layers with a thickness of 90 m. No sub-layering was  
314 applied to the U1 unit as its thickness is only around 100 m. Finally, we applied a lithological switch  
315 at two uppermost layers in order to account for MDAC deposits, that mimics the appearance of these  
316 particular lithofacies after deposition. The final static model is composed of 39 depositional events and  
317 one litho-switch event (Fig. 3, Table 1).

#### 318 *Boundary Conditions*

319 In order to model the thermal evolution through time, a lithosphere model was created with varying  
320 bottom boundary conditions. The three main elements that characterize the lithosphere (upper crust,  
321 lower crust and upper mantle) were taken from publications (Artemieva and Thybo 2013; Brunet  
322 1994; Brunet 1997). The base of the upper mantle is assumed to be the base of the model, defined by  
323 the 1333°C mantle isotherm representing the Lithosphere-Asthenosphere Boundary (LAB) and was  
324 digitized from Artemieva and Thybo (2013). Two rifting events experienced by the Bay of Biscay  
325 (Ferrer et al. 2008; Tugend et al. 2014; Brunet 1994; Desegaulx and Brunet 1990) were defined to  
326 model heat flow variations in the geological past. The rifting is initiated from a McKenzie-type crustal  
327 model with an instantaneous (less than 20 My) stretching of the lower and upper crust (McKenzie  
328 1978). Then, the subsidence of the basin is simulated using extension coefficients ( $\beta$ -factor) from  
329 Brunet (1997):  $\beta = 1.2$  for the Triassic rift event and  $\beta = 1.4$  for the Upper Jurassic rift event.

330 The upper thermal boundary is defined as a surface temperature map at the top of the model for each  
331 geological time step using the *Paleo-latitude calculator for Paleoclimate study* from van Hinsbergen  
332 et al. (2015) and the equivalent diagram from Wygrala (1989) which require paleo-latitudes of the  
333 basin over time. Since temperatures at the sea-bottom are usually much cooler compared with onshore  
334 environments at the same latitude (Dembicki 2016), the sea bottom surface temperature was corrected  
335 for paleo-bathymetry using the method described in Toole (1981). This resulted in a series of  
336 temperature maps, one for each geological event, that were imposed at the top of the model and that  
337 account for the changing latitude and bathymetry of the basin.

338 *Biogenic source rock definition*

339 Biogenic gas generation of a given source rock occurs between 10 and 100°C (Katz et al. 2011) and is  
340 determined as a function of thermal gradient (°C/km) and sedimentation rate (m/My) (Schneider et al.  
341 2016). An optimal heating rate at deposition time ranges between 7°C/My and 18°C/My (Clayton,  
342 1992) (Fig. 4).

343 The thermal gradient and sedimentation rate maps were computed by the TemisFlow® simulator and  
344 multiplied to determine the heating rate maps at deposition time for each layer (Fig. 5a-c). These maps  
345 were then converted into biogenic potential index maps that determine the areas in which any OM may  
346 be converted to microbial CH<sub>4</sub> (Fig. 5d).

347 Five potential source rock layers in the Plio-Pleistocene series and one potential source rock in the  
348 Miocene sediments presented optimal conditions for biogenic gas generation. Their input geochemical  
349 parameters (e.g. TOC and HI) were taken from the Rock-Eval analysis (Table S1).

350 *Concepts of modelling biogenic gas generation and migration processes*

351 Published OM degradation models (Westrich et al. 1984; Janssen 1984; Middelburg 1989; Middelburg  
352 et al. 1996; Canuel and Martens 1996; Boudreau and Ruddick 1991; Robinson and Brink 2005; Arndt  
353 et al. 2013) are the results of experimental laboratory studies, performed at human time scales and at  
354 specific thermal conditions. A basin model however needs to represent the time span of the entire  
355 geological history of a basin and its thermal evolution. A general modelling approach is needed that  
356 accounts for the main biogenic gas production processes but that can also be applied at different  
357 geological space and time scales.

358 Our modelling approach considers the total initial Sedimentary Organic Matter (SOM) is composed of  
359 TOClab, TOCzlab and TOCbio-ref. The labile TOClab is (Eq. 1, Fig. 2) the part of the OM that is  
360 immediately degraded at the moment of deposition according to the degradation law of Middelburg  
361 (1989) which is a function of OM reactivity ( $R_{bio}$ ) and microbial activity ( $\mu(T)$ ) (Eq. 1). This model  
362 describes an exponential decrease of the OM with depth and time and leads to a strong degradation in  
363 the first few meters of the sedimentary column. This shallow depth is challenging in basin simulators  
364 where the vertical resolution of layers is usually in the range of tens to hundreds of meters. In addition,  
365 all hydrocarbons generated or migrated in the uppermost layer are assumed lost to the surface. Under  
366 these conditions, only the fraction of TOClab at greater depth would be capable of generating biogenic  
367 gas. In order to account for a higher fraction of the biodegradable OM, a thermogenic source of labile  
368 TOC is introduced in our conceptual model (Burdige 2007; Burdige 2011). It is represented by the  
369 thermo-labile part (TOCzlab) of the initial TOC and corresponds to the OM that can be trapped and  
370 protected in the mineral matrix during the first stages of diagenesis (Burdige 2011). When temperature  
371 increases, TOCzlab can turn into labile OM which is sensitive to biodegradation. This process releases

372 new labile compounds later in time and results in an additional generation of biogenic gas at greater  
 373 depth. The transformation of TOCzlab is modelled using a first-order kinetic cracking scheme (Eq. 2).  
 374 For a continental-derived OM, composed mainly by waxes of higher plants (Largeau and  
 375 Vandenbroucke 2007; Kamga 2016), the generation of methane at low temperature is mainly the result  
 376 of the degradation of the aliphatic portions (*e.g.* long fatty acids) (Kamga 2016) considered as the most  
 377 thermo-labile compounds with low activation energy. The third and last fraction of the initial TOC  
 378 (TOCbio-ref) is bio-refractory and corresponds to the TOC fraction that is used in traditional  
 379 petroleum systems analysis. TOCbio-ref is not sensitive to microbial activity and is converted into  
 380 hydrocarbons by thermogenic cracking reactions only. In this study, TOCbio-ref values are derived  
 381 from Rock-Eval analysis (see Table 3).

382 Thus, the total initial SOM is defined as the sum of these three fractions (Fig. 2):

$$383 \quad \text{Total Initial SOM} = \text{TOCbio-ref} + \text{TOClab} + \text{TOCzlab}$$

384 TOClab evolution through time follows a continuous degradation law (Eq. 1):

$$\frac{\partial \text{TOClab}}{\partial t} = -R_{\text{bio}} * (a_{\text{bio}} + t)^{-b} * \mu(T) * \text{TOClab} - \frac{\partial \text{TOCzlab}}{\partial t} \quad (1)$$

385 where  $R_{\text{bio}}$  represents a dimensionless calibration parameter linked to the sedimentary environment. A  
 386 default value of 0.16 is derived from Middelburg (1989).  $a_{\text{bio}}$  is the apparent initial age of the OM  
 387 (Ma),  $t$  the time of the degradation process (Ma) and  $b$  is equal to 0.95 (Middelburg 1989).  $\mu(T)$  ( $^{\circ}\text{C}$ ) is  
 388 the temperature dependent function of microbial activity derived from Belyaev et al. (1983).

389 TOCzlab degradation is defined by a first order kinetic reaction (Eq. 2):

$$\frac{\partial \text{TOCzlab}}{\partial t} = -k(T) * \text{TOCzlab} \quad (2)$$

390 where reactivity  $k$  is defined by the Arrhenius law (Eq. 3):

$$-k(T) = A * e^{-\frac{E_a}{RT}} \quad (3)$$

391  $T$  represents the temperature (K),  $E_a$  the activation energy ( $\text{kJ mol}^{-1}$ ),  $R$  the universal gas constant  
 392 ( $8.3144621 \text{ J.mol}^{-1}.\text{K}^{-1}$ ) and  $A$  the frequency factor ( $\text{s}^{-1}$ ).

393 The final generated biogenic gas is derived from the transformation of the labile organic carbon  
 394 fraction whose biogenic  $\text{CH}_4$  generation rate ( $\tau_{\text{bio}}$ ) (Eq. 4) is defined as:

$$\tau_{\text{bio}} = -\frac{m_{\text{CH}_4}}{m_{\text{C}}} * s_{\text{bio}} * \frac{\partial \text{TOClab}}{\partial t} \quad (4)$$

395 where  $m_{\text{CH}_4}$  = methane molar mass,  $m_{\text{C}}$  = carbon molar mass and  $s_{\text{bio}}$  = stoichiometric coefficient  
396 controlling the amount of organic carbon which is converted to microbial methane.

397 In conclusion, biogenic methane is directly generated by the labile TOC fraction following two steps  
398 (Fig. 2): first, the labile TOC fraction is transformed into methane, and then the thermo-labile TOC is  
399 transformed at greater depth into labile TOC that is afterwards converted into additional methane.

400 Once the biogenic gas is generated, it is subject to the following processes (in order of priority): (1)  
401 adsorption by the organic matter following the Langmuir law, which quantifies the capacity of the OM  
402 to adsorb methane as a function of temperature and pressure; (2) dissolution in formation water  
403 following an equation of state (EOS) which is a function of pressure, temperature and salinity, and  
404 subsequent advective transport in the water phase (Duan et al. 1992); (3) migration in a separate vapor  
405 phase following multi-phase Darcy's law.

406 Biogenic gas can also be accumulated in structural or stratigraphic traps in a vapor phase, or as a solid  
407 phase in the form of gas hydrates (Brothers et al. 2014; Johnson et al. 2015; Skarke et al. 2014). In the  
408 Aquitaine Basin, however, temperature and pressure conditions are not conducive to gas hydrate  
409 deposits (Dupré et al. 2020). The absence of hydrates over geological time is also confirmed by our  
410 numerical simulations.

#### 411 *Quantitative sensitivity analysis*

412 As mentioned in the introduction, the values of the model parameters, and especially those describing  
413 the biogenic gas generation process, are uncertain. Sensitivity analysis can be performed to estimate  
414 the impact of these parameters on the modelled processes and to determine those that are the most  
415 critical. This can help to better understand the processes involved in the biogenic gas production and  
416 migration and to simplify the calibration process by focusing on the relevant parameters.

417 Here we performed a variance-based global sensitivity analysis to quantify the influence of the  
418 parameters on the output of interest (Sobol' 1990). More specifically, input parameters are considered  
419 to be independent random variables with given probability distributions. Indices are then computed  
420 that quantify the impact of the parameter uncertainty on the output variance. The main (or first-order)  
421 effect measures the part of the output variance explained by the parameter alone. It ranges between 0  
422 and 1. The total effect, as defined in Homma and Saltelli (1996), estimates the global sensitivity of the  
423 output to the parameter. The difference between the total and main effects corresponds to interactions  
424 between the studied parameter and some other parameters.

425 The estimation of the main and total effects requires knowing the value of the output of interest for a  
426 very large number of models. To avoid such a computational overburden, we consider here meta-  
427 models that mimic the simulator. More precisely, we generate a sample of the parameter space and

428 perform the corresponding simulations. This provides a set of basin models, the training set, that is  
429 used to approximate the relationship between the input parameters and the output of interest, providing  
430 fast estimations of this output for any parameter values (Wendebourg 2003; Feraille and Marrel 2012).  
431 If these estimations are accurate enough, they can replace the calls to the simulator during the  
432 computation of the sensitivity indices. To check the quality of the meta-model estimations, we  
433 consider here an additional sample of the parameter space, independent from the training set, and  
434 compare the output simulated values for these new models with those predicted by the meta-model.  
435 The resulting errors are gathered in the R2 correlation index (see Gervais et al. (2018) for more  
436 details).

437 This workflow has already been used in a variety of contexts. In what follows, meta-models are built  
438 by kriging interpolation, and are combined with reduced-basis decomposition to predict the spatial  
439 distribution of properties in the basin as described for instance in Gervais et al. (2018).

## 440 **5. RESULTS**

### 441 *Organic Matter Characterization*

442 As mentioned above, to characterize the OM we collected cuttings at depths ranging from 595 to 1530  
443 m from the Pelican-1 and Pingouin-1 wells located in the offshore Parentis Basin. At the same depth  
444 and formation interval, the two wells showed different TOC values (Table 1S). Pingouin-1 is  
445 characterized by a very low OM content which an overall decrease with depth ranging from 0.44% in  
446 the shallower Plio-Pleistocene to 0.32% TOC in the Miocene. The Pelican-1 well shows higher OM  
447 content, with TOC values principally ranging from 0.44% to 0.47% respectively from the top Plio-  
448 Pleistocene to the base Miocene. Only one sample (PELICAN-7) is characterized by a higher TOC  
449 value of around 10.35% which is probably due to the presence of black OM in vitrinite residues  
450 already observed and described in Michel (2017). Otherwise, the samples show OI values between  
451 ~240 and 500 mgCO<sub>2</sub>/gTOC and very low HI ( $\leq 55$  mg HC/gTOC) suggesting an altered continental-  
452 derived OM (Fig. 6). A mean Tmax value of 420°C indicates that the OM is immature.

### 453 *Thermal and pressure regime*

454 Calibration of present-day temperatures was obtained by modifying thermal conductivities of  
455 lithologies in each strata in accordance with those given in Pasquale et al. (2011). Calibration results  
456 are shown in Figure 7. A lithospheric model (section 4) constrained the thermal evolution of the basin  
457 through time which was calibrated with vitrinite reflectance data from 6 wells (Fig. 8). Note that in  
458 this study, we do not model any deeper thermogenic petroleum systems as those known in the offshore  
459 Parentis Basin as we focus on Cenozoic strata within which the biogenic gas source rocks are found.  
460 According to the calibrated model, the Miocene layer reaches its maximum temperature between 32

461 and 45°C at the present day. These temperatures also correspond to the microbial activity peak and  
462 optimal conditions for the generation of microbial gas (Katz et al. 2011). Note also that vitrinite  
463 measurements were reported without any description of the rock samples from which they were taken  
464 adding to the uncertainty of the final paleo-temperature history.

465 Pressure measurements indicate some overpressure in the basin: Pelican-1 encountered an  
466 overpressure of 6.28 MPa at 3125 m in a shaly horizon, Antares-1 encountered a small overpressure of  
467 1.78 MPa at 2056 m (Figure 1S). Hydrostatic pressure gradients depend on salinity. The water  
468 composition offshore Aquitaine is highly variable, probably related to the presence of large salt  
469 accumulations and extensive diapirism. Salinities encountered in Pelican-1 show a mean value of 65  
470 g/l  $\pm$  15 at 1823-1860 m depth (Paleocene), a mean value of 150/180 g/l at 2500 m (Aptian), and  
471 values up to 145 g/l at 2800 m (Barremian). Salinities from the Antares-1 well show lower values at  
472 similar depths (56 g/l at 2567 m). Despite such a high variability of water salinity, pressure calibration  
473 was achieved with a mean water salinity of 50 g/l.

#### 474 *Sensitivity Analysis on biogenic gas generation*

475 As mentioned previously, the parameters describing the biogenic gas generation are not completely  
476 known for continental-derived terrestrial type III-OM in the Aquitaine Basin. We thus performed a  
477 sensitivity analysis on 7 input parameters likely to have a significant impact on biogenic gas  
478 generation in the offshore Aquitaine: TOClab, TOCzlab,  $R_{\text{bio}}$ ,  $E_a$ ,  $\mu(T)$ ,  $S_{\text{bio}}$  and water salinity.

479 Ranges of kinetic parameters are based on published data for a type III organic matter (Middelburg  
480 1989; Hedges and Oades, 1997; Martens and Canuel al. 1996; Burdige 2007, 2011) and on previous  
481 modelling work of biogenic gas generation (Ducros and Wolf 2014; Ducros et al. 2015). As presented  
482 in Burdige (2011 and reference therein), the activation energy ( $E_a$ ) for recent organic matter can vary  
483 between 50 to 130 kJ/mol. In our case study, biogenic gas generation is favorable when  $E_a$  is  
484 comprised between 80-110 kJ/mol. Higher or lower value prevent the biogenic gas generation. We  
485 therefore reduced the range proposed in Burdige (2011) as proposed in Table 2. Here, we did not  
486 consider the frequency factor ( $A$ ) of the TOCzlab kinetics (Eq. 3) as a critical parameter. Indeed, it is  
487 well known that, for the same reactivity, variations in  $E_a$  can be compensated by  $A$  (Peters et al.  
488 2018). In accordance with previous kinetic studies (Behar et al. 1997; Dieckmann 2005; Schenk et al.  
489 1997) we fixed  $A$  and varied  $E_a$  in the range of published data to find an optimal kinetic law for  
490 TOCzlab. However, in order to more accurately describe the degradation of a recent type-III OM and  
491 reduce uncertainty, further research should focus on the analytical assessment of the molecular  
492 composition of a recent continental-derived organic matter.

493 The perturbation of the  $\mu(T)$  function is performed through the variation of the temperature  
494 corresponding to the peak of maximum activity instead of varying the function as presented in Table



495 2. Water salinity was included in the sensitivity analysis to assess its impact on methane dissolution  
496 rather than on the final amount of generated gas. The ranges of variation of all the critical input  
497 parameters are given in Table 2.

498 To estimate the sensitivity indices, a Latin Hypercube sample of 100 models was generated (McKay et  
499 al. 1979) and used to get first qualitative results.

500 Since the migration of microbial gas evolves as a function of the total amount of generated gas (SQG,  
501 Fig. 9), special attention was given to the sensitivity of SQG to the uncertain parameters. Figure 10  
502 shows the value of SQG for the 100 models of the sample as a function of  $E_a$ ,  $s_{bio}$  and  $R_{bio}$ . We can  
503 observe a negative correlation between SQG and the activation energy ( $E_a$ ), as well as a positive  
504 correlation for both  $s_{bio}$  (Fig. 10a,b) and low values of  $R_{bio}$  (Fig. 10c). No clear trend can be observed  
505 for the other parameters.

506 The results of the variance-based sensitivity analysis on SQG are presented in Figure 11. The meta-  
507 models used to compute these total and main effects were derived from the 100 models and quality-  
508 checked using 50 additional models. Parameters  $E_a$ ,  $s_{bio}$  and  $R_{bio}$  appear to be the most influential on  
509 SQG, while the proportion of labile versus thermo-labile compounds in the OM (TOClab and  
510 TOCzlab) seems to have only a limited impact. This may be related to the quite small range of  
511 variation chosen for these fractions.

512 If we now consider in more details the spatial distribution of parameters  $E_a$ ,  $s_{bio}$  and  $R_{bio}$  total effect on  
513 SQG in the layers (Fig. 12), we can observe some variability depending on the source rock horizon.

514 The impact of  $E_a$  is strongest in the Miocene source rock and decreases in the shallower Plio-  
515 Pleistocene layers (Fig. 12). This is probably due to degradation rates for the thermo-labile part of the  
516 OM that increase with temperature (Eq. 3) and thus with depth. As a result, the variability of  $E_a$  has  
517 more impact at greater depth. The same trend is visible for  $s_{bio}$ : the influence on SQG increases with  
518 depth, with a higher impact on the deeper Miocene source rock compared with the uppermost Plio-  
519 Pleistocene sediments (Fig. 12). This result is probably linked to the higher organic carbon availability  
520 in the deeper source rock, derived from the total transformation of both TOClab and TOCzlab, which  
521 is then converted to biogenic methane as function of  $s_{bio}$  (Eq. 4). The results for  $R_{bio}$  show the opposite  
522 behavior: the impact is strongest in the uppermost layers where TOClab is the most sensitive to  
523 degradation, and small in the deeper layers (Fig. 12).

524

### 525 *Scenario for microbial gas generation*

526 In our model, each source rock layer, from the deeper Miocene to the shallower Plio-Pleistocene, is  
527 defined by a constant TOCbio-ref determined from Rock-Eval analysis (Table 3). The degradation

528 laws for the labile compound and the kinetic laws for the thermo-labile fraction are identical for each  
529 source rock layer. We use the estimation of the gas flux in the northern area identified by Dupré et al.  
530 (2020) to constrain these laws. More specifically, the difference between the total mass of generated  
531 gas and the total mass of gas in place (either adsorbed, dissolved or free) provides us an estimation of  
532 the amount of gas lost at the seafloor, and thus an estimation of the gas flux which can be compared to  
533 the flux measured by Dupré et al. (2020) in the northern area. The optimal value among the set of  
534 models is obtained for the input parameters values given in Table 2 (“This study” column). We can see  
535 that it requires a low activation energy of 83 kJ/mol, which is necessary to activate the thermo-labile  
536 TOC fraction at low temperatures as in the case of the Plio-Pleistocene source rocks. This model is  
537 considered in what follows as our reference scenario.

538 With this scenario, the average per-area amount of generated gas is 78 kg/m<sup>2</sup> (Fig. 13) which amounts  
539 to 25.5 Gt/My when integrated over time along the entire area of ~1188 km<sup>2</sup> (Fig. 14). The highest  
540 microbial gas amount is generated by the upper Miocene source rock which reached its highest  
541 temperature (~ 32°C) at the present day. Methane is first generated by the initial labile fraction during  
542 early diagenesis but continues to be generated by other labile molecules derived from the  
543 transformation of TOC<sub>zlab</sub> with increasing temperature. The area of maximum generation is localized  
544 along the shelf edge where the sediment thickness is the highest resulting in both higher burial and  
545 temperature. Generation decreases along the upper slope where no fluid activity has been identified  
546 (Dupré et al. 2020) (Figs. 1, 14). Part of this generated gas is adsorbed to the source rock, or dissolved  
547 in the pore water, or trapped as a free gas when saturations are high enough. As shown in Figure 13,  
548 biogenic gas is mainly present in the system as dissolved in water. Formation water is almost always  
549 under-saturated with respect to CH<sub>4</sub> and a free methane phase is minimal in the uppermost layers  
550 mainly at the shelf break (Fig. 13d). Dissolved gas moves driven by hydrodynamic gradients. As  
551 compaction is the main driving force, water flow is mainly vertical and therefore methane flux is also  
552 mainly vertical, from the source rock to the seafloor. However, flow in the uppermost strata is  
553 impacted by MDAC deposits which prevent gas to easily escape to the seafloor. The modelled gas  
554 migrates upwards along a narrow N-S oriented strip near and east of the shelf break (Fig.14) where gas  
555 generation rate and sediment permeability are most favorable.

556 Once the fluid reaches the seafloor, methane is exsolved as a free gas phase. Our results suggest that  
557 gas seeps at the seabed may be principally linked to gas diffusion close to the water/sediment interface  
558 rather than from large quantities of free gas migrating to the surface. Considering the difference  
559 between the total mass of generated and in place gas (either adsorbed, dissolved or free), we estimate  
560 that the amount of gas lost at the seafloor is 0.91 Gt/My over an area of ~107 km<sup>2</sup> which corresponds  
561 to the gas flux in the northern area modelled after Dupré et al. (2020) (Fig. 14).

## 562 6. DISCUSSIONS

### 563 *Cumulative volume of released microbial methane at the seafloor in the Aquitaine Shelf*

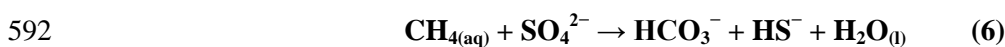
564 Dupré et al. (2020) estimated an amount of emitted methane over the Aquitaine Shelf of 144 Mg/yr  
565 based on measurements from local bubbling sites (Ruffine et al. 2017) and acoustic water column  
566 signatures of escaping gas bubbles. Our study area is restricted to the northern Aquitaine Shelf (see  
567 location in Fig. 1b) and corresponds to 1.88 Tcf/My (Trillion Cubic Feet per million years) (Dupré et  
568 al. 2020).

569 Our model indicates a total mass of generated microbial methane of 25.5 Gt/My over 5.53 My  
570 corresponding to the time since the beginning of the generation process. At the maximum generation  
571 depth (mean depth ~1100 m), the deeper source rock is at P-T conditions of ~ 10 MPa and ~ 35°C  
572 where CH<sub>4</sub> density is 72 kg/m<sup>3</sup> using the AGA8 equation of state (ISO 12213-2 2006; Starling and  
573 Savidge 1992) (Fig. 15). Thus the total volume of generated gas is 3.55\*10<sup>+5</sup> Mm<sup>3</sup>/My (equivalent to  
574 12.8 Tcf/My).

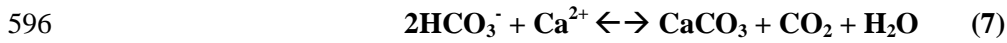
575 At the water depth range of emission sites, P-T conditions are 2.6 MPa and 10°C resulting in a gas  
576 density of 19.7 kg/m<sup>3</sup> (Fig. 15). Based on a gas loss of 0.91 Gt/My, we can estimate the cumulative  
577 volume of emitted gas as 4.63\*10<sup>+4</sup> Mm<sup>3</sup>/My (equivalent to 1.62 Tcf/My).

578 MDAC pavements represent a sink of CH<sub>4</sub>. At the edge of the Aquitaine Shelf, they are associated  
579 with microbial methane seeps which are oxidized in the Anaerobic Methane Oxidation zone to CO<sub>2</sub>  
580 (Pierre et al. 2017). During upward migration, the generated methane meets the SO<sub>4</sub><sup>2-</sup> of the downward  
581 diffusing seawater in the Sulphate-Methane Transition Zone where it is consumed by the activity of  
582 methanotrophic archaea with SO<sub>4</sub><sup>2-</sup> reducing bacteria (Boetius 2000; Conrad 2005; Thauer 2010; Lash  
583 2015) in anoxic conditions. Note that we did not account for the sulfate-reduction of organic matter as  
584 it is one of the process less likely to induce local authigenic carbonate precipitation compared to the  
585 AOM (Paull and Ussler 2008). In addition, extensive precipitation of MDACs within the subsurface, is  
586 usually related to SMTZ occurring at shallower sub-bottom depths (e.g. < 20 mbsf) (Paull and Ussler  
587 2008 and reference therein) which can be the case of the Bay of Biscay (Pierre et al. 2017, Dupre et al.  
588 2020). Here, we assume that in the Bay of Biscay the AOM is the driving process for MDAC  
589 precipitation.

590 The AOM redox reaction can be described as the net reaction between seawater sulfate and methane  
591 (Eq. 6):



593 The dissolved inorganic carbon (bicarbonate) generated in the STMZ under anaerobic conditions  
594 increases alkalinity that promotes carbonate precipitation resulting in the formation of authigenic-  
595 carbonate (Eq. 7) (Boetius 2000; Regnier et al. 2011; Lash 2015).



597 This process is a widespread diagenetic reaction along modern continental margins (Reeburgh 2007,  
598 Lash 2015) where part of the generated methane is consumed before it reaches the seafloor (Regnier et  
599 al. 2001). Therefore, methane oxidation during upward migration should also be taken into account to  
600 model biogenic gas processes. However, the integration of this process in basin modelling is  
601 complicated by the fact that the AOM thickness is very small, around 2 m within the STMZ, and  
602 occurs at variable shallow depths.

603 Based on the current knowledge from the offshore Aquitaine (Dupré et al. 2020), we can estimate the  
604 average amount of CH<sub>4</sub> consumed through the AOM. Using a mass balance approach, the CO<sub>2</sub>  
605 “trapped” in MDAC is 43% of the total molar mass of CaCO<sub>3</sub>. The exact thickness of the MDAC  
606 outcropping and sub-cropping is unknown but with information from seismic data (Fig. 1, Dupré et al.  
607 2020), we can estimate a variable thickness of 2 to 10 m which is discontinuous along the shelf.  
608 Considering an extent of MDAC of 200 km<sup>2</sup> (Fig. 14), we can determine an average volume of  
609 MDAC. Assuming an average thickness of 5 m for the MDAC, we can estimate the amount of CO<sub>2</sub>  
610 stored in the carbonates which corresponds to the total amount of CH<sub>4</sub> consumed through AOM.

611 The total mass of consumed CH<sub>4</sub> (mCH<sub>4</sub>) through the AOM can be defined as (Eq. 8):

$$612 \quad m\text{CH}_4 = \rho * V * f \quad (8)$$

613 where  $\rho$  is the CaCO<sub>3</sub> density (2700 kg/m<sup>3</sup>),  $V$  is the CaCO<sub>3</sub> volume (m<sup>3</sup>) and  $f$  is the molar fraction of  
614 CO<sub>2</sub> trapped as MDAC equal to 43%. Note that we are assuming that all CO<sub>2</sub> both in the system and  
615 trapped in the MDAC derives from methane oxidation only.

616 To convert the total CH<sub>4</sub> mass (Eq. 8) to total gas volume, we consider that at the emission water depth  
617 the gas density is 19.7 kg/m<sup>3</sup> (Fig. 15) resulting in 5.89\*10<sup>+4</sup> Mm<sup>3</sup> of CH<sub>4</sub> (2.06 Tcf) that is trapped in  
618 MDAC. This means that 23% of the uprising methane is consumed through AOM resulting in a  
619 reduced total emission rate of 1.25 Tcf/My. Note that if we consider a lower limit of MDAC thickness  
620 of 2 m, the emission rate is 1.48 Tcf/My corresponding to 9% of CH<sub>4</sub> consumed through AOM. In  
621 contrast, a higher thickness of 10 m results in 0.87 Tcf/My of microbial CH<sub>4</sub> emitted at the seafloor,  
622 corresponding to 46% of CH<sub>4</sub> trapped in MDAC.

623 ***Modelled present-day flow rates of microbial methane***

624 The modelled hydrodynamic regime of the northern Aquitaine Basin is shown in Figure 16. During  
625 compaction, porosity loss induces vertical water expulsion (Fig. 16a, b). In our model, most of the gas  
626 is dissolved in the formation water (Fig. 13) in the upper layers that are characterized by  
627 unconsolidated sediments with high porosity (modelled values between 50 and 60%) (Fig. 16a, b).  
628 Therefore, we can approximate the methane flux to the vertical water flux. We also observe that the  
629 low porosity of MDAC at the seafloor acts as a barrier preventing the water to circulate easily up to  
630 the water-sediment interface (Fig. 16a). Migration and expulsion processes are then controlled by the  
631 hydrodynamic regime of the upper part of the basin in which methane migrates to the seafloor as a  
632 function of sediment geometry, permeability and water flux.

633 Our model indicates methane in a free gas phase whenever gas saturation is reached in the water. This  
634 condition is sensitive to the amount of free water in the layer, P-T conditions and amount of generated  
635 gas. Basin modelling grids are limited by their spatial resolution. Layer thickness and cell size can  
636 impact the amount of free water in the system. Gas saturation is reached when gas generation or  
637 pressure conditions are high enough to exceed the solubility threshold or when layer thickness is  
638 sufficiently small which reduces the amount of free water. In our model, we observe that the majority  
639 of the gas is dissolved in water due to gas saturation that is decreasing during upward migration  
640 caused by AOM. Indeed, in the Aquitaine Shelf, MDACs represent the main sink for CH<sub>4</sub> and  
641 therefore imply that gas remains dissolved in water up to the seafloor where it diffuses due to  
642 changing thermodynamic conditions at the seafloor. Given the high permeability of the upper  
643 unconsolidated sediments (Fig. 16 b), we can assume that the total gas released at the present day is  
644 proportional to the water flow through the uppermost layer.

645 Due to the absence of capillary pressure, it is not possible to accumulate hydrocarbons in the  
646 shallowest layer. Thus, we calculated the water flow through the second-last layer as follows (Eq. 9)

$$\mathbf{Methane\ Flux} = \frac{[\mathbf{CH4}]_{tf} - [\mathbf{CH4}]_{ti}}{tf - ti} \quad (9)$$

647 where ti corresponds to the last geological event defined in the model (0.14 Ma) and tf to the present  
648 day. As shown in Figure 16, gas is migrating upward to the seafloor along the Aquitaine Shelf edge  
649 but no such activity is observed on the slope (Dupré et al. 2020; Michel et al. 2017). Variations of  
650 methane concentration in water have been computed for several grid cells and integrated over the  
651 northern study area (Fig. 1b) which yields an average methane flow rate of 27 Mg/y (Fig. 17). This  
652 number has the same order of magnitude as the estimated methane flow rate of 35 Mg/y from in situ  
653 flow rate measurements and acoustic data (Dupré et al. 2020).

654 In our model, the total mass of emitted methane yields a methane flux of 23 mgCH<sub>4</sub>/m<sup>2</sup>/y over the  
655 northern Aquitaine surface (Fig. 1b). Present-day methane flow rates have also been compared with  
656 paleo-flow rates. We computed concentration changes of dissolved gas in water between the  
657 deposition of the first Plio-Pleistocene source rock at 2.87 Ma and the following geological event ( $\Delta t =$   
658 0.23 My). The average amount of emitted methane in that time interval reaches 11 Mg/y  
659 corresponding to 9.8 mgCH<sub>4</sub>/m<sup>2</sup>/y. In contrast, the deposition of the last source rock layer at 1.76 Ma  
660 and the following geological event ( $\Delta t = 0.19$  My) results in a methane flow rate of 41 Mg/y  
661 corresponding to 35 mgCH<sub>4</sub>/m<sup>2</sup>/y, which turns out to be the maximum modelled methane flux through  
662 the seafloor. Therefore, present-day flow rates are relatively smaller because all the source rocks are  
663 already deposited and the more “mature” Miocene source rock had already generated a large part of its  
664 labile potential resulting in a higher flux in the past compared to what we currently observe. This  
665 result is probably due to the absence of sediments above the Plio-Pleistocene source rocks during time  
666 of deposition (1.76 Ma), where the gas can easily escape through the seafloor compared to the present  
667 day where gas migration is controlled by an overburden and its permeability. Thus, gas migration over  
668 time along the offshore Aquitaine Shelf edge evolves as a function of variable generation and  
669 sedimentation rates.

670 Note that in our study, we did not take into account a probable input from a Holocene source rock as  
671 proposed in Dupré et al. (2020). Indeed, in our model, the Holocene layers are too shallow (between  
672 150 to 200 m of water depth along the shelf) to act as a probable biogenic source rock. We can also  
673 assume that its contribution to the final cumulative volume of generated/emitted gas would be low  
674 compared to any deeper source rock.

## 675 **7. CONCLUSIONS**

676 This study presents for the first time an attempt to quantify the total amount of emitted biogenic gas at  
677 the seafloor over time, applied to the Aquitaine Shelf. Along with a calibrated basin model,  
678 geochemical results from Rock-Eval and quantitative sensitivity analysis, we propose a model for the  
679 evolution of the microbial methane system in the sediments of the offshore Aquitaine Basin.

680 A global sensitivity analysis based on meta-models helped to identify the most critical parameters for  
681 gas generation. Given the uncertainty ranges for the input parameters, methane production appears  
682 mainly controlled by the reactivity of the OM rather than by the relative percentage of labile and  
683 thermo-labile compounds. The final amount of generated microbial methane strongly depends on the  
684 deposition age of the source rock. In our model, all source rocks depleted their thermo-labile fraction  
685 that is defined by a low activation energy. Only the shallower and more recent Plio-Pleistocene source  
686 rocks still have a labile potential to generate biogenic gas compared to the older and deeper Miocene

687 source rock that is totally depleted. However, a dedicated analytical assessment of the reaction kinetics  
688 and reactivity of the OM is required in order to more accurately assess OM degradation.

689 The generated gas is mainly present in the system as dissolved in water migrating vertically until it is  
690 finally released as a separate gas phase at the seafloor. Migration pathways are controlled by sediment  
691 permeability and by maximum generation rates along the shelf. This system seems to be active since  
692 the first source rock was deposited in the Messinian, with a mean modelled methane flow rate of 11  
693 Mg/y until the deposition of the last source rock during the early Pleistocene where it reaches a  
694 maximum emission rate of 41 Mg/y when all source rocks were deposited without any further  
695 sedimentation and the gas was easily released at the seafloor. Modelling results also show that present-  
696 day methane flow rates (27 Mg/y) are in the same order of magnitude than flow rates estimated from  
697 in situ flow rate measurements and acoustic data (35 Mg/y) (Dupré et al. 2020). Our results confirm  
698 that the absence of a seal at the top of the system resulted in continuous methane emission over time  
699 along the offshore Aquitaine Shelf edge and CH<sub>4</sub> flow rate intensities evolved as function of microbial  
700 methane generation and sedimentation rates.

701 Our modelling approach demonstrates that a gas system originating from only microbial activity can  
702 be active over millions of years generating significant methane volumes that depend on the specific  
703 geological setting. In our 3D model, the mass of generated gas over time corresponds to 25.5 Gt/My of  
704 biogenic CH<sub>4</sub>. The difference between the total mass of generated methane and the total mass still in  
705 place (in either adsorbed, dissolved or free state) yields a loss of 0.91 Gt/My. However, part of this gas  
706 is not directly released at the seabed but rather oxidized into CO<sub>2</sub> through AOM during upward  
707 migration. Based on MDAC thickness variation of 2 - 10 m and assuming that all CO<sub>2</sub> present in the  
708 system is sourced by methane oxidation only, we could determine an average amount of consumed  
709 CH<sub>4</sub> through AOM varying between 9% and 46% of the initial generated methane volume. Thus, the  
710 average volume of emitted gas over time along the Aquitaine Shelf ranges between 0.87 Tcf/My and  
711 1.48 Tcf/My. This result demonstrates that if we want to better understand and estimate the total  
712 amount of emitted methane and its impact on the ocean/atmosphere carbon budget, we need to account  
713 for (1) the total amount of generated gas, (2) the total amount of trapped gas in the system and (3) the  
714 total amount of consumed gas through the AOM.

715 In this study, we present a new workflow to assess biogenic gas occurrences in continental shelf  
716 settings at the basin scale where microbial CH<sub>4</sub> is sourced from recent continental-derived OM. This  
717 new approach, applied and calibrated to the offshore Aquitaine, can help estimate the total CH<sub>4</sub>  
718 emitted naturally from shallow-water shelf areas that may reach the atmosphere. This subject is of  
719 particular interest for the scientific community working on the impact of global warming issues as  
720 methane is a major greenhouse gas with a negative contribution on climate and environment.

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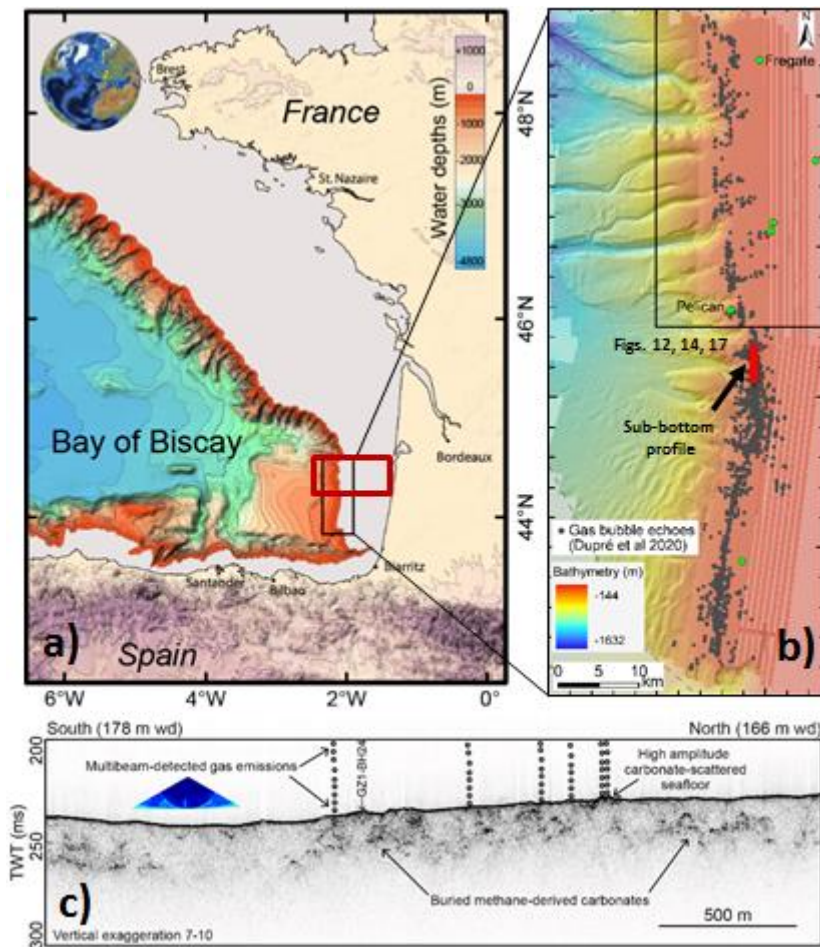
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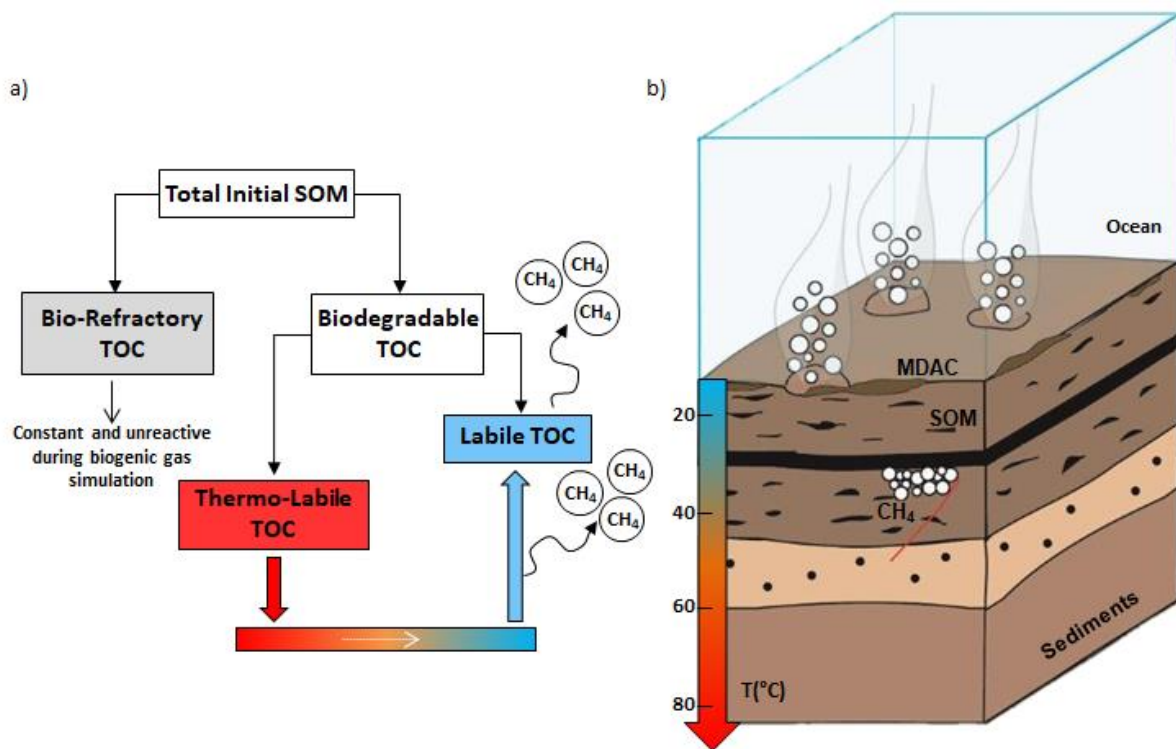
1078 **Figure 1.** a) Bathymetric map of the Bay of Biscay (Southwestern France) and modelled area (red rectangle) of Fig. 3  
 1079 modified after Sibuet et al. (2004) and Dupré et al. (2020); b) Detailed shaded bathymetric map offshore Aquitaine  
 1080 (Loubrieu 2013, Gazcogne1) with gas emission site distribution and localization of the sub-bottom profile (red line)  
 1081 shown in Fig. 1c and the modelled offshore area in Fig. 1b (black rectangle) (modified after Dupré et al. 2020); c) Sub-  
 1082 bottom profile acquired in the emission site showing the presence of sub-cropping methane-derived authigenic  
 1083 carbonates from Dupré et al. (2020).

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1089 **Figure 2. a) Schematic diagram of the microbial gas generation concept. The gas is generated during the early**  
 1090 **diagenesis stage by the labile TOC. At greater burial and depth, the transformation of the thermo-labile TOC allows**  
 1091 **to produce new labile fraction that generate new gas. The bio-refractory TOC is non-reactive and constant during**  
 1092 **biogenic gas simulation but it can be transformed into hydrocarbons by thermogenic cracking at greater temperature**  
 1093 **(> 80°C). b) Schematic block diagram offshore Aquitaine.**

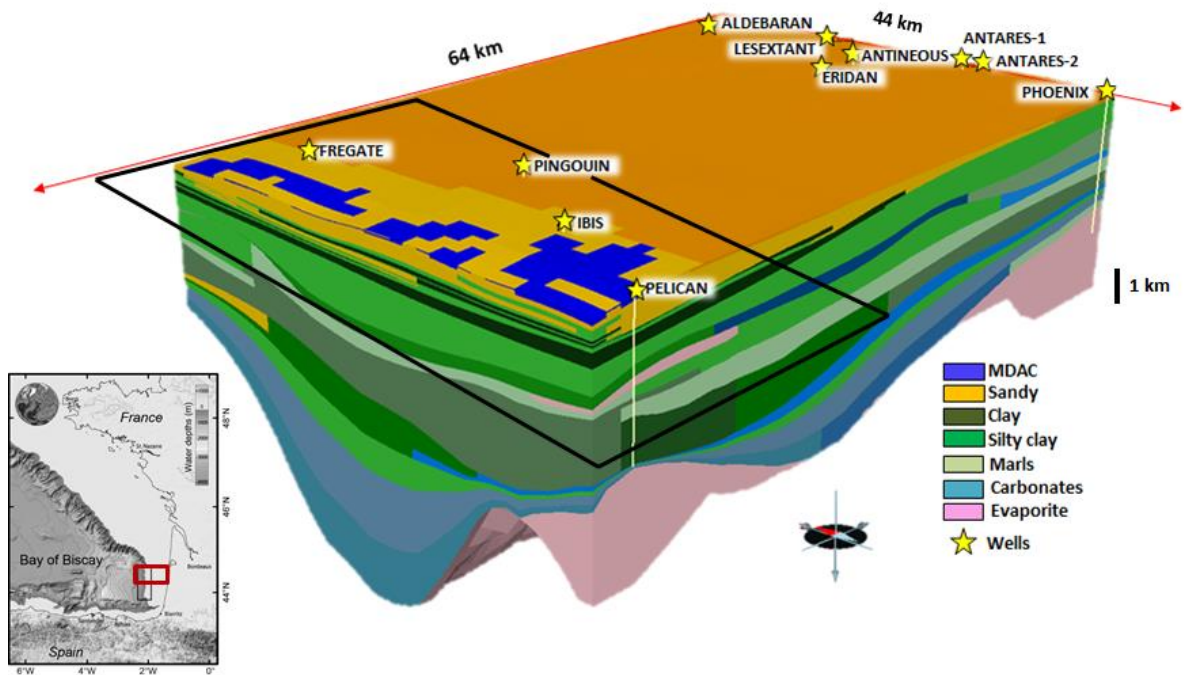
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1100 **Figure 3.** 3D block diagram of the study area from TemisFlow®. The model covers an area of ~2800 km<sup>2</sup> representing  
 1101 a shelf part of the offshore Aquitaine Basin (red rectangle) (Fig. 1a) where seeps have been mapped (black rectangle)  
 1102 (Fig. 1b) with in situ measurements and annual estimation of methane flow rates (Dupré et al. 2020). The black  
 1103 rectangle represents the extent of maps in Figs. 12, 14 and 17.

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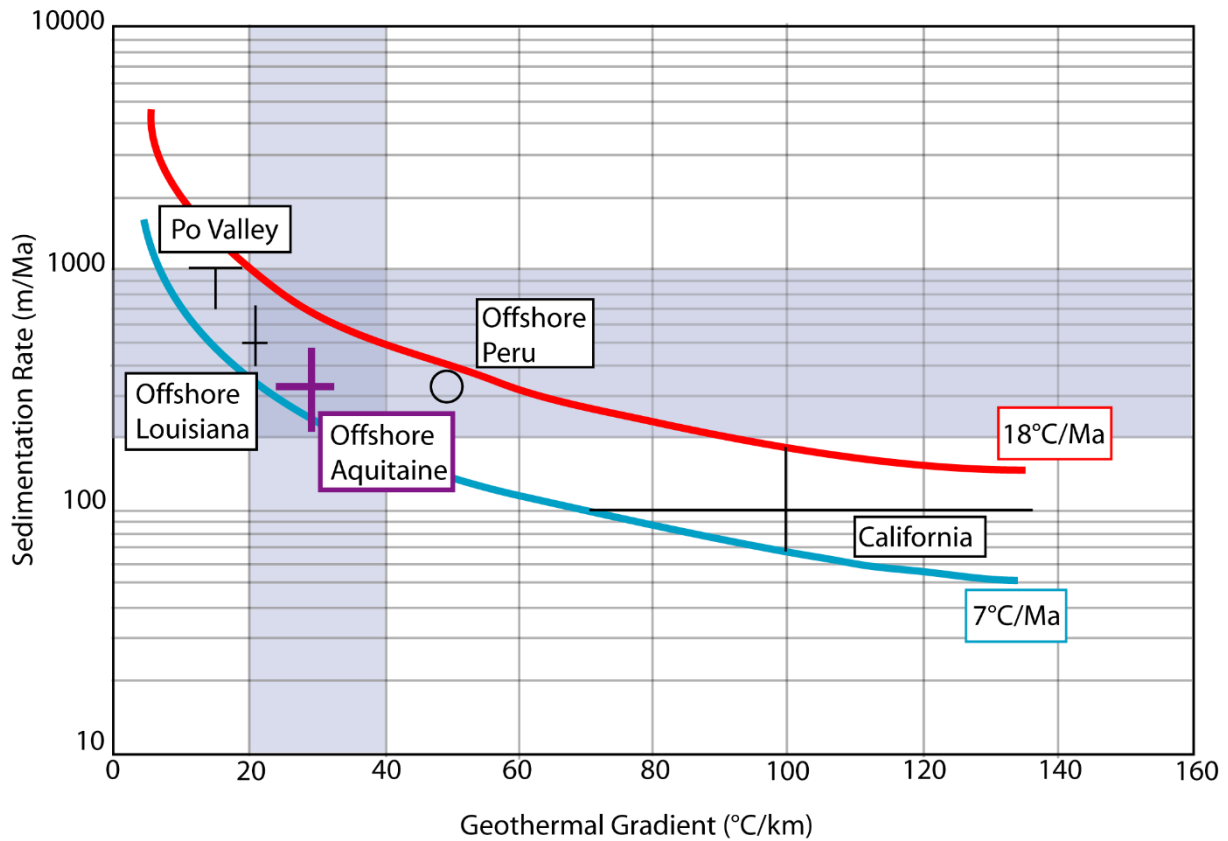
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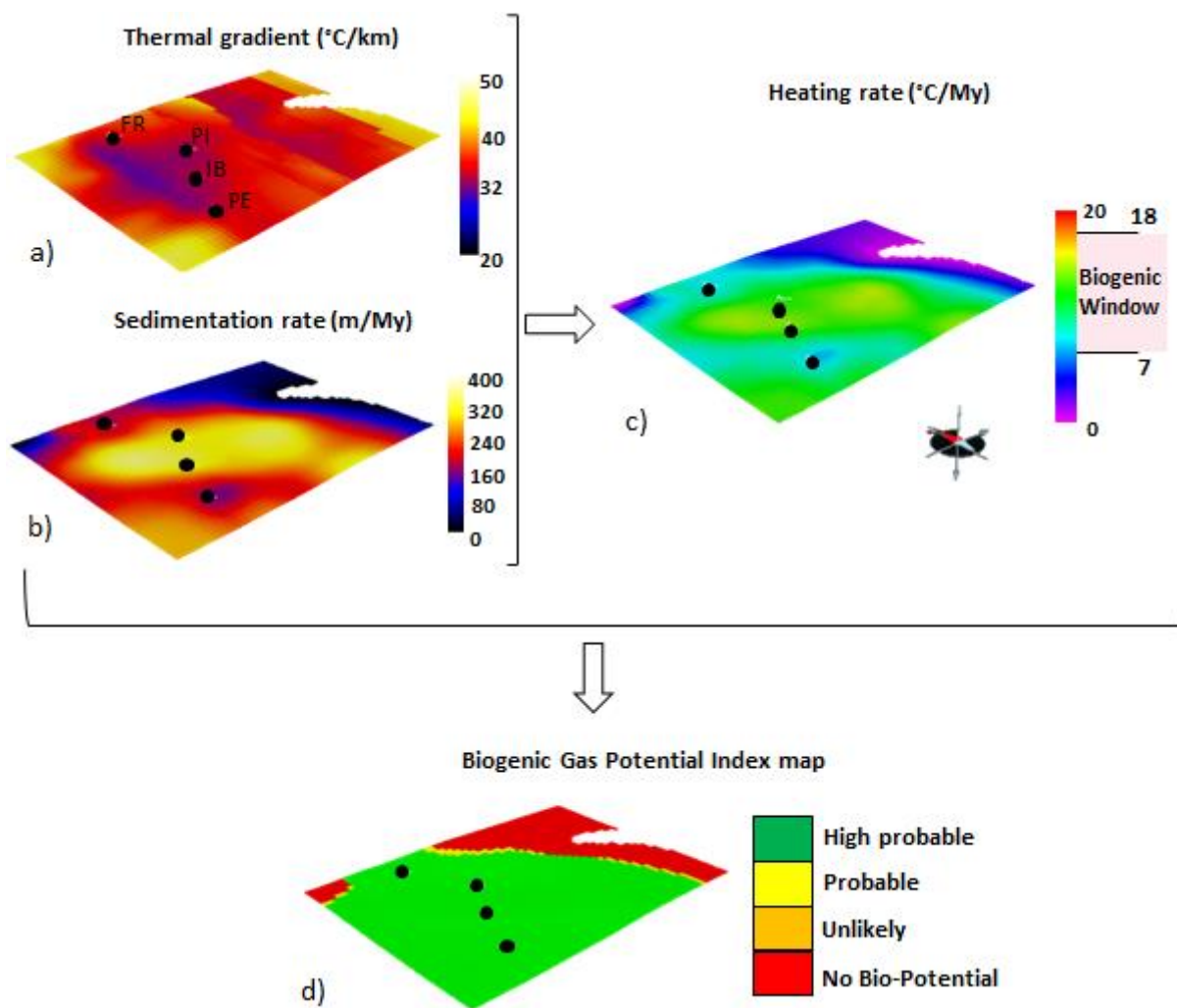
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Figure 4. Biogenic gas maturity windows based on the heating rate which is determined as a function of the sedimentation rate over the geothermal gradient (modified after Clayton 1992). The highlighted area indicates the normal geothermal gradient and sedimentation rate for worldwide sedimentary basins (Clayton 1992). In the offshore Aquitaine, the Plio-Pleistocene sequences are characterized by favorable conditions for biogenic gas generation (purple lines).



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1140 Figure 5. The thermal gradient (a) and the sedimentation rate maps (b) computed in TemisFlow® are multiplied to  
 1141 obtain the heating rate map (c). This map is then converted into a “Biogenic Gas Potential Index” map (d) to  
 1142 determine the areas entering the biogenic maturity window in which any OM may be converted into microbial  
 1143 methane for the upper Miocene layer. Black dots represent offshore wells (FR – Fregate-1; PI – Pingouin-1; IB – Ibis-  
 1144 1; PE – Pelican-1) (for well locations see Fig. 3).

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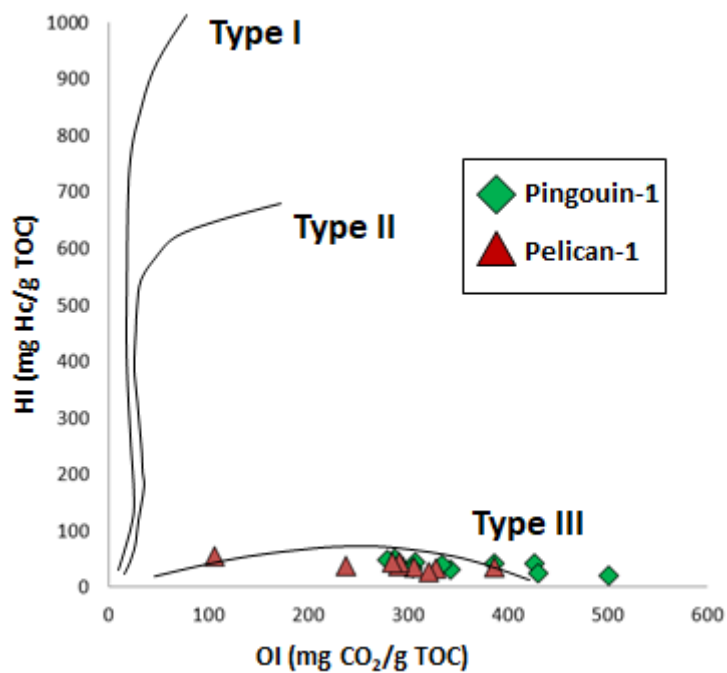
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1155 Figure 6. Rock-Eval results on cuttings collected from Pelican-1 and Pingouin-1 wells offshore Aquitaine. Well  
 1156 locations are displayed in Figure 3. The OM derives from continental origin (Type III). The samples are mainly  
 1157 characterized by poor TOC content (see Table S1) and very low HI values.

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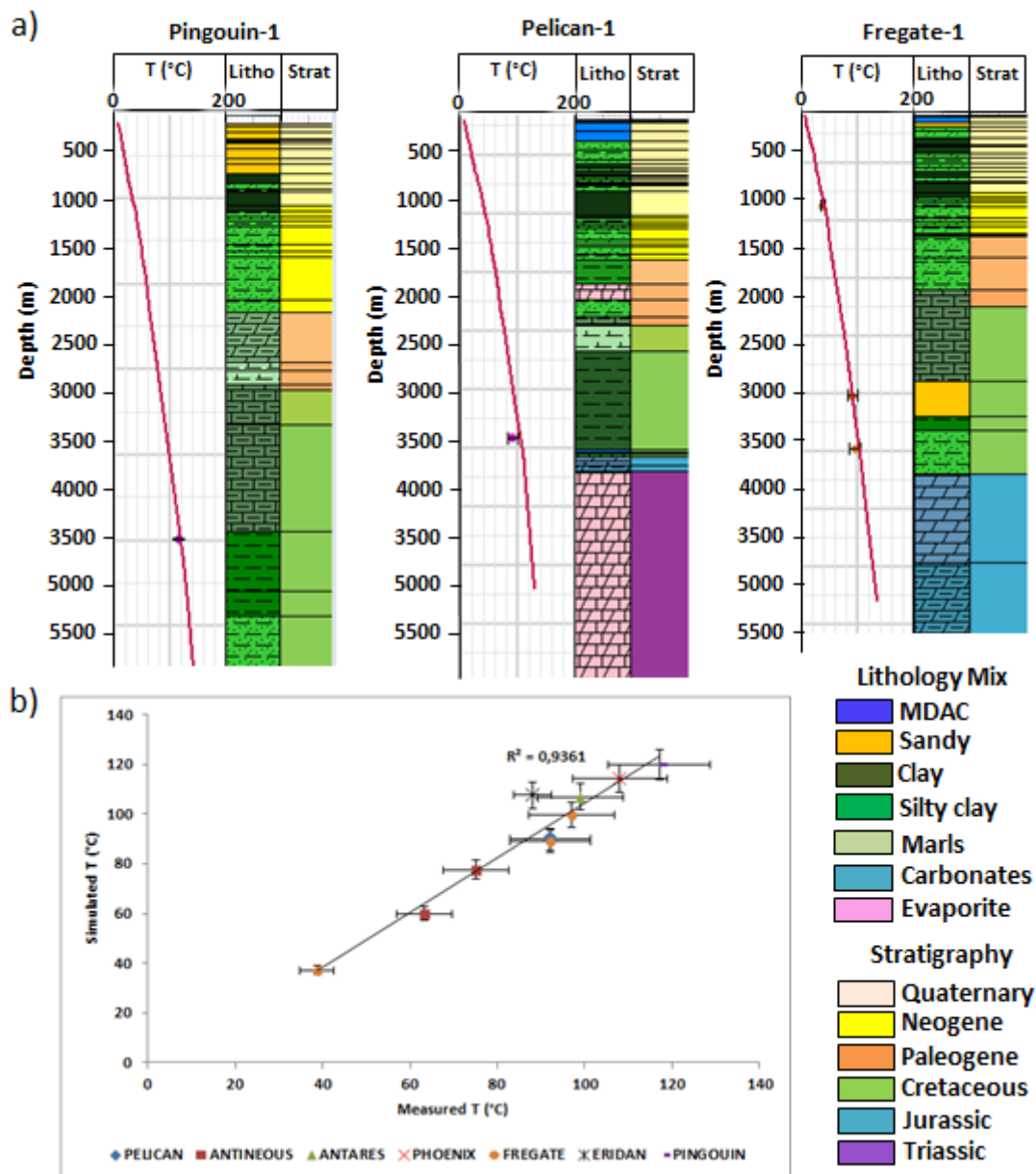
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1169 Figure 7. a) Present-day temperature calibration results for 3 wells located offshore Aquitaine with corresponding

1170 stratigraphy and lithology used in the 3D model. b) Temperature calibrations for all 7 wells are given by a cross-plot

1171 “Simulated vs Measured Temperatures”. Well locations are shown in Figure 3.

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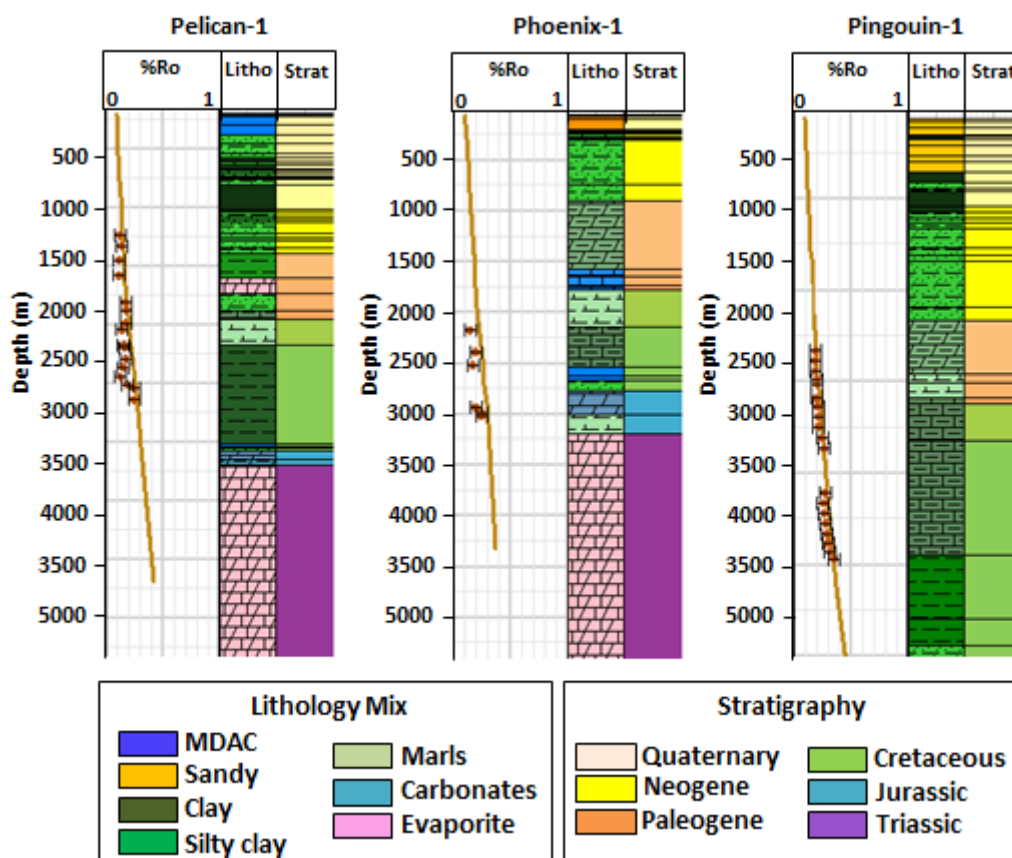
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1185 Figure 8. Paleo-thermal calibration of vitrinite reflectance data for 3 of the 6 wells of the Aquitaine Basin with  
1186 corresponding stratigraphy and lithology used in the model. The modelled maturities (orange curves) show a good fit  
1187 with measured vitrinite reflectance values for all wells, staying within the standard deviation. Well locations are  
1188 shown in Figure 3.

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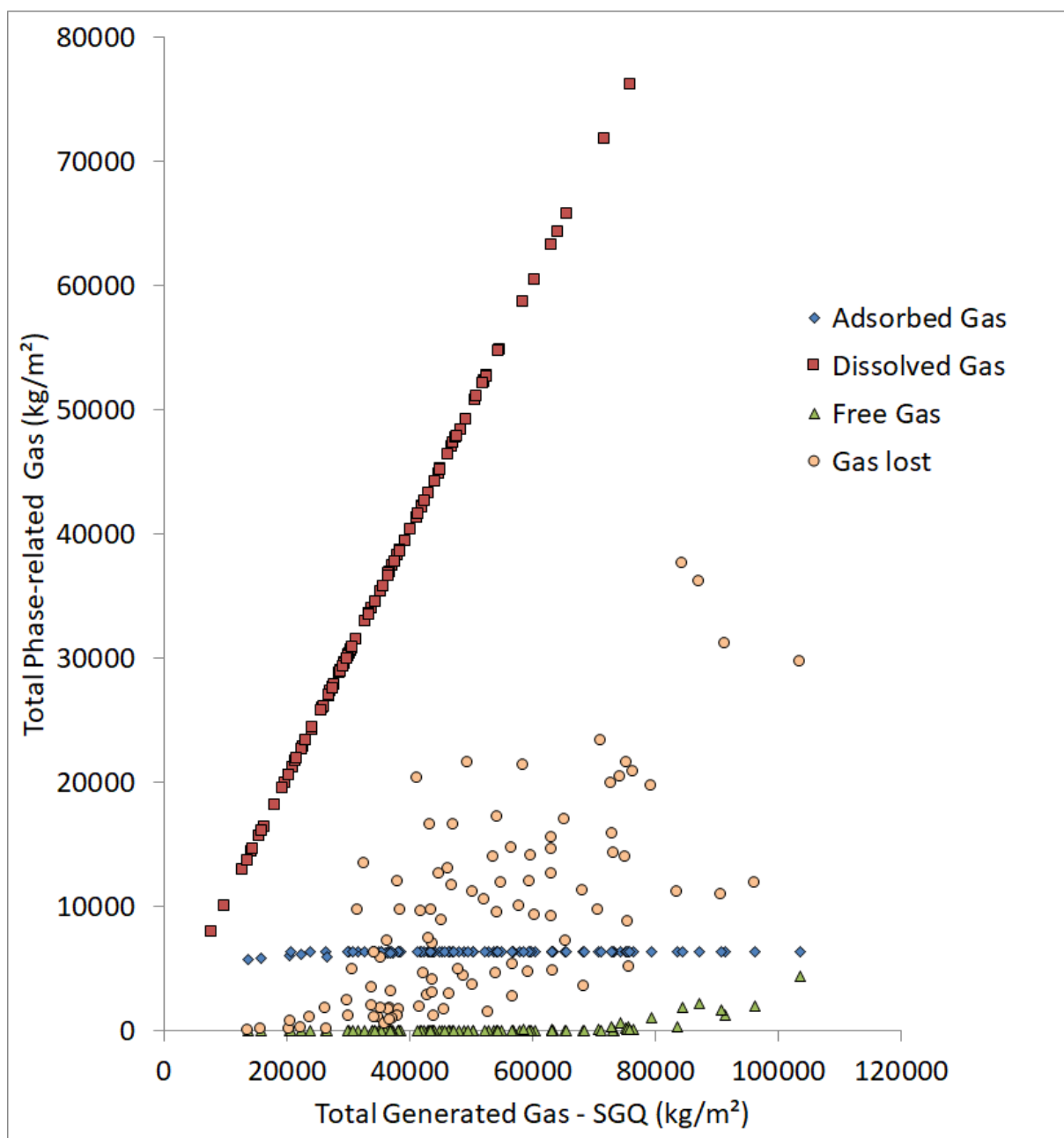
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1197 **Figure 9. Microbial gas phase behavior as function of the total generated gas (SGQ) based on a set of 100 simulations**  
 1198 **sampling the uncertain parameter space. The gas can be free in the system only when water becomes saturated. The**  
 1199 **total amount of gas lost at the surface increases as the cumulative generated gas increases.**

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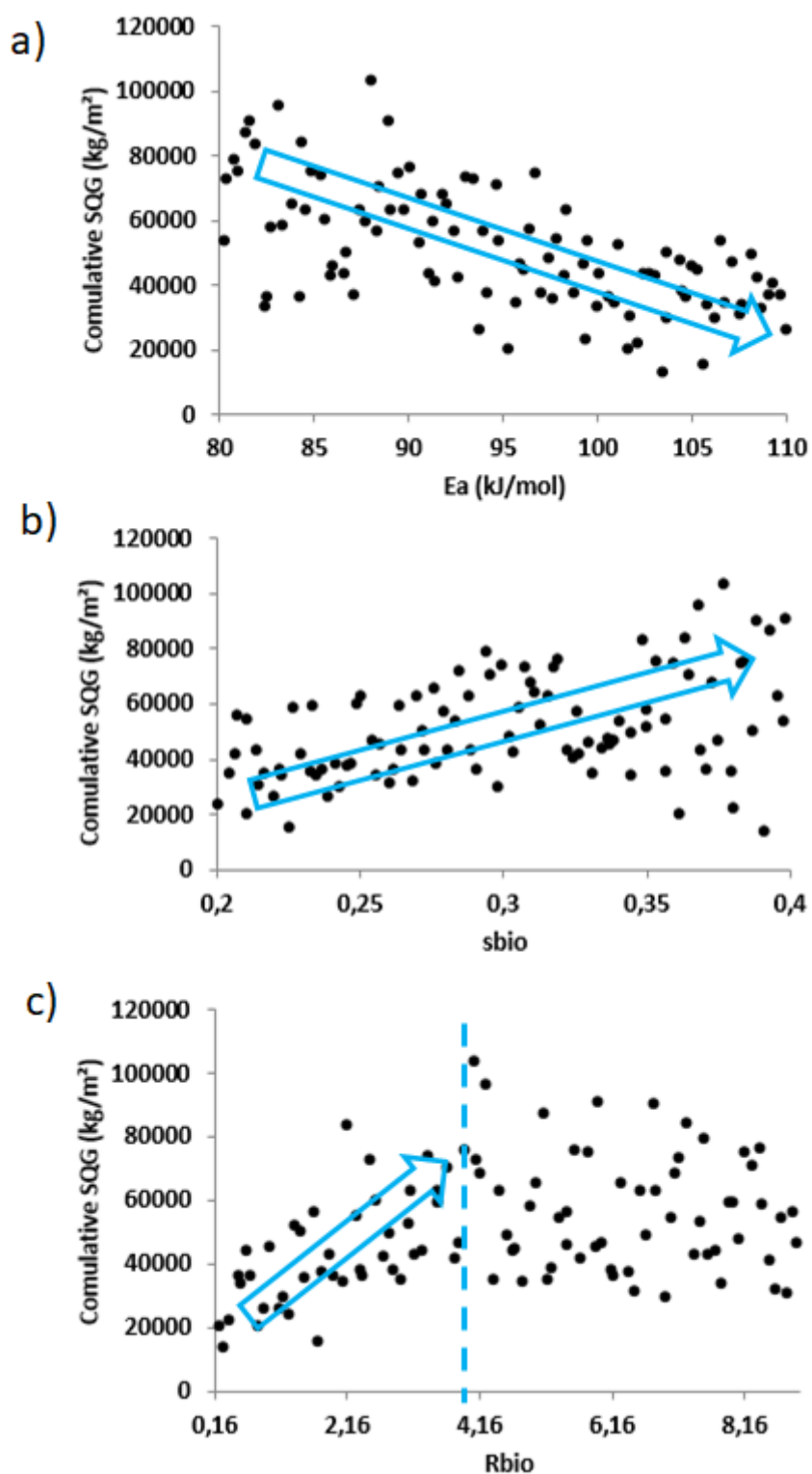
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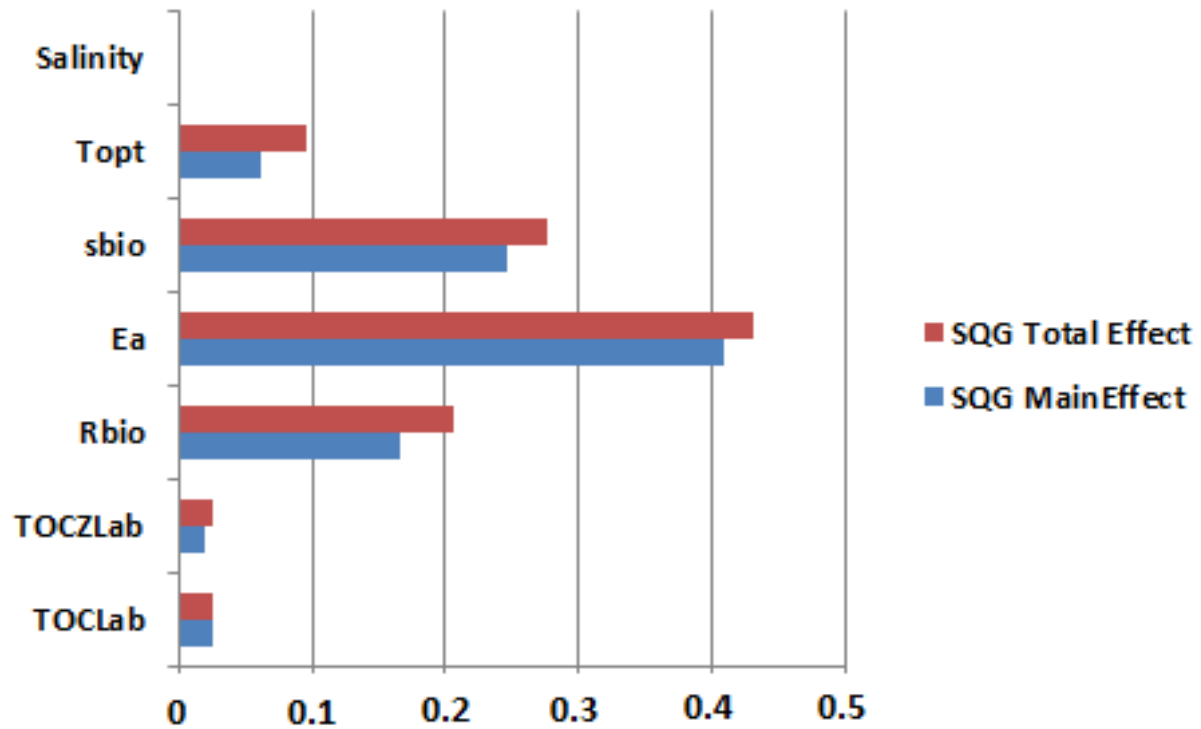
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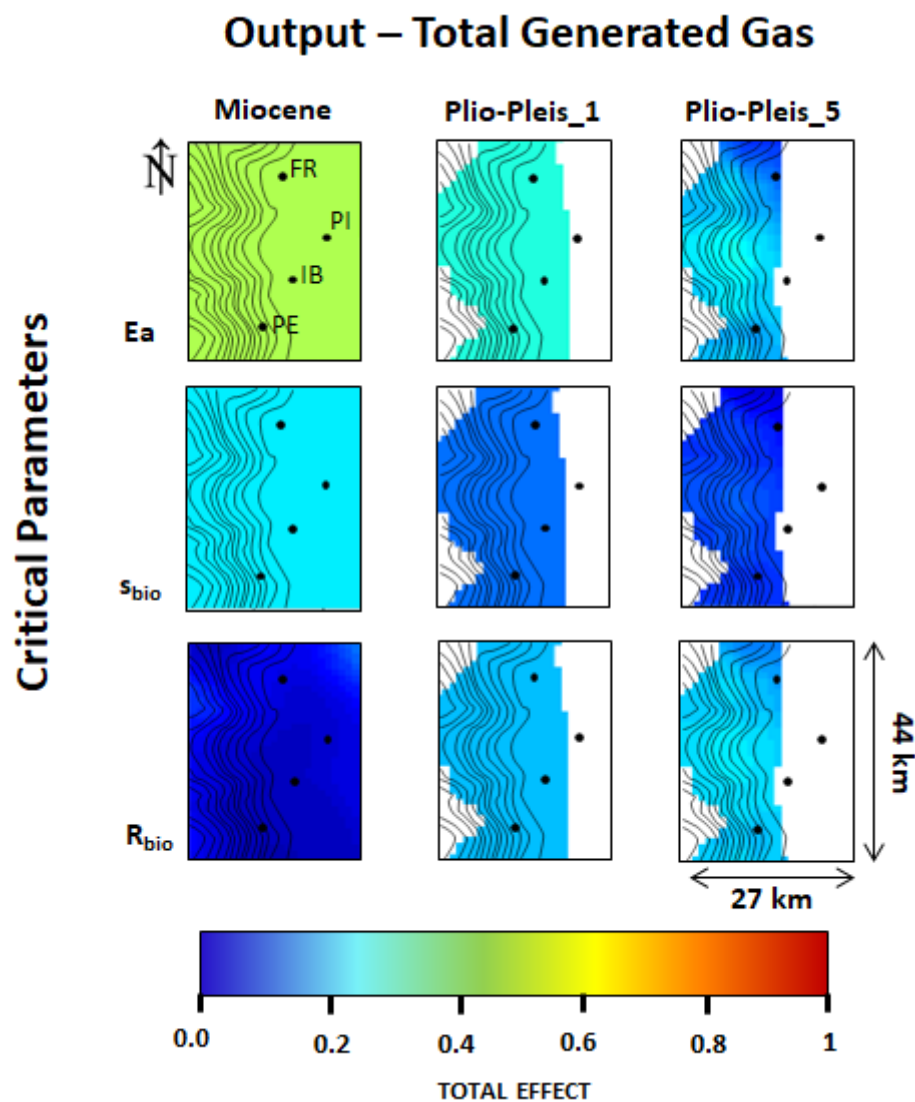
1210 Figure 10. Total amount of generated gas (SQG) as function of three critical parameters for the 100 simulations of the  
 1211 training set. The SQG property shows some positive correlation with  $S_{bio}$  and some negative correlation with  $E_a$ .  
 1212 Some correlation is also visible for values of  $R_{bio}$  lower than 4. No clear trend can be observed between SQG and any  
 1213 other parameter.



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1215 Figure 11. Total and main effects on the total generated gas (SQG) computed for the 7 uncertain parameters. The  
 1216 small differences between the two effects highlight that, in our case study, there are no significant interactions  
 1217 between the parameters that affect the generation of methane. SQG is mainly impacted by Ea,  $s_{bio}$  and  $R_{bio}$   
 1218 parameters, in order of priority.

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1221 Figure 12. Total effect obtained for the three main influential parameters ( $E_a$ ,  $s_{bio}$ ,  $R_{bio}$ ) on three of the six source rock  
 1222 layers (Table 3) over the northern studied area (see location in Fig. 1b). Black dots represent the offshore wells (FR –  
 1223 Fregate-1; PI – Pingouin-1; IB – Ibis-1; PE – Pelican-1) (Figs. 1, 3 and 5). Black lines represent the seafloor  
 1224 bathymetry with a contour interval of 50 m.

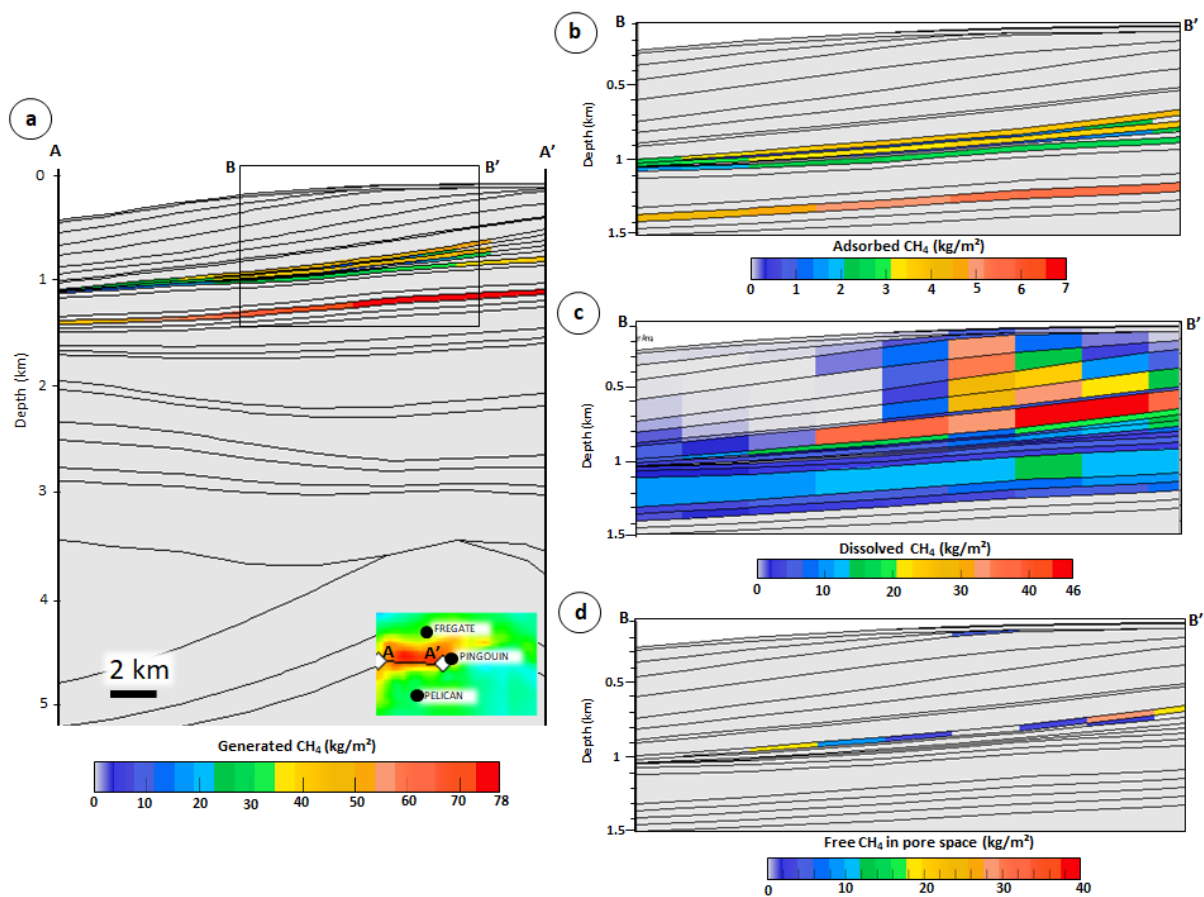
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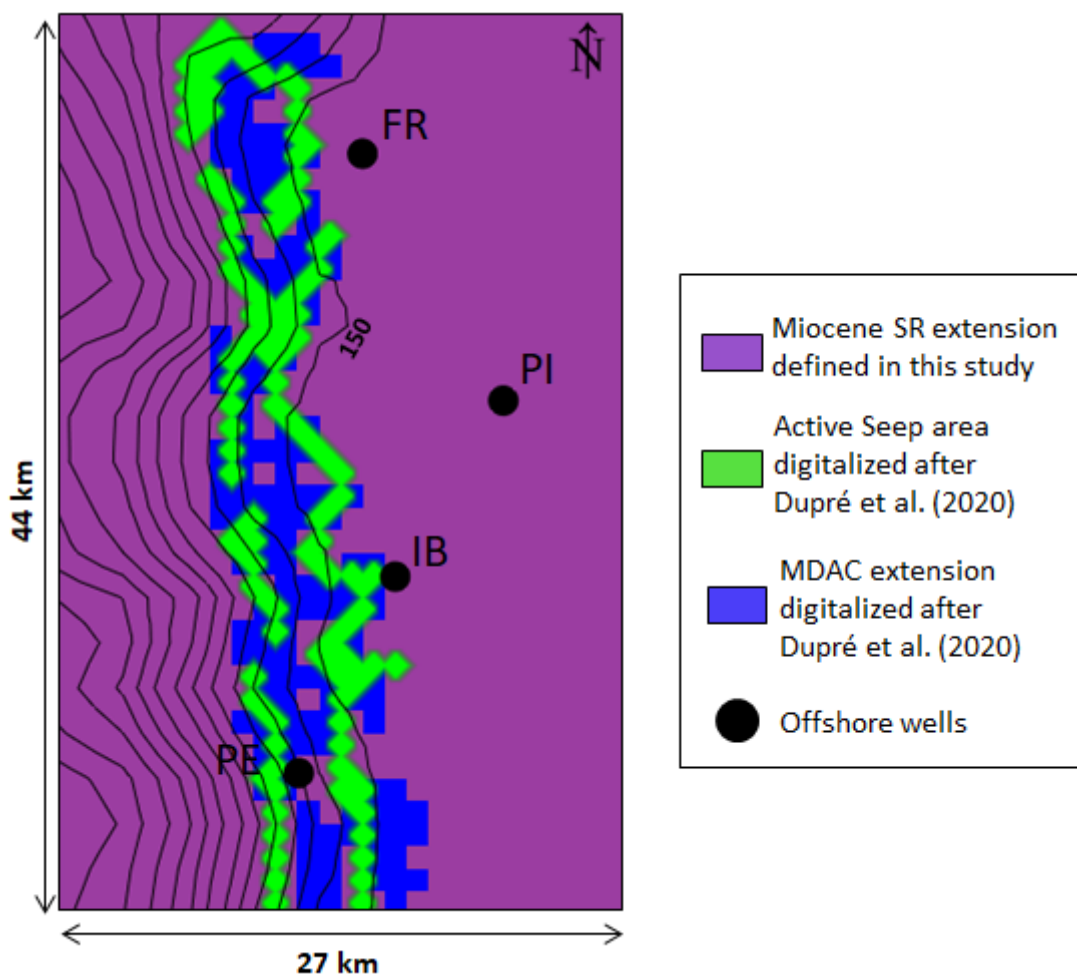
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1231 **Figure 13. 2D sections across the basin model (profile AA') showing mass of a) the generated gas from biogenic**  
 1232 **production per area and b-d) mass of gas in place per area at the present day, with b) total mass of gas adsorbed in**  
 1233 **the organic matter; c) total mass of gas dissolved in formation water; and d) total mass of free gas in pore space.**

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1236 **Figure 14. Map of Miocene Source Rock (SR) defined in this study with extent of seeps and MDACs digitized from**  
 1237 **Dupré et al. (2020) over the northern study area (see map location in Fig. 1b). The location of the offshore wells (FR –**  
 1238 **Fregate-1; PI – Pingouin-1; IB – Ibis-1; PE – Pelican-1) is given in Figs.1 and 3. Black lines represent the seafloor**  
 1239 **bathymetry with a contour interval of 50 m.**

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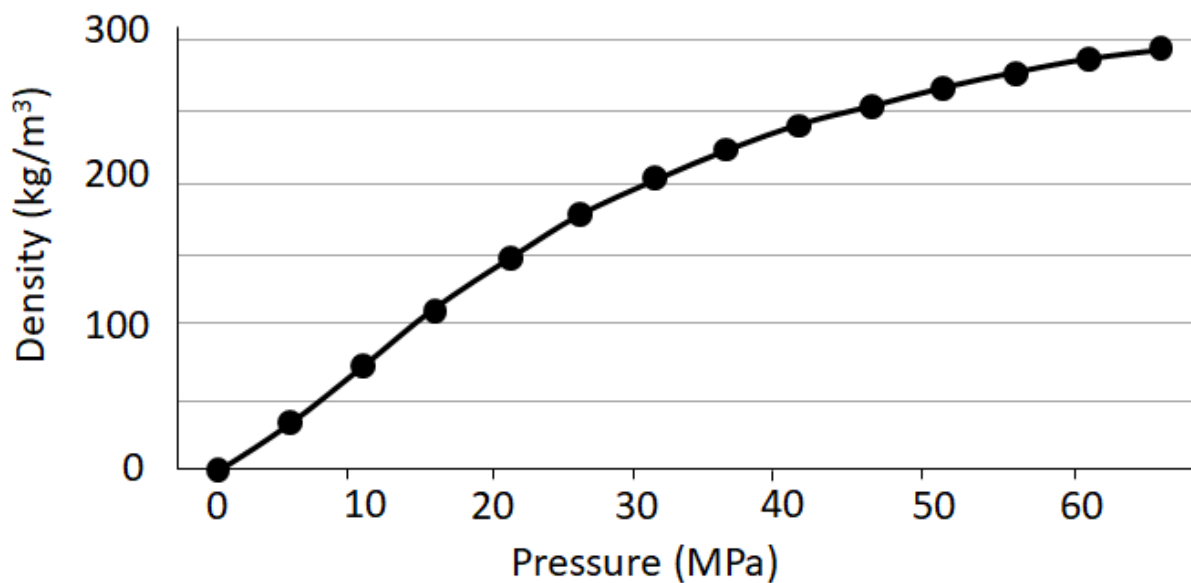
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1254 Figure 15. Methane density as function of pressure using the AGA8 equation of state (ISO 12213-2, 2006; Starling and  
1255 Savidge1992).

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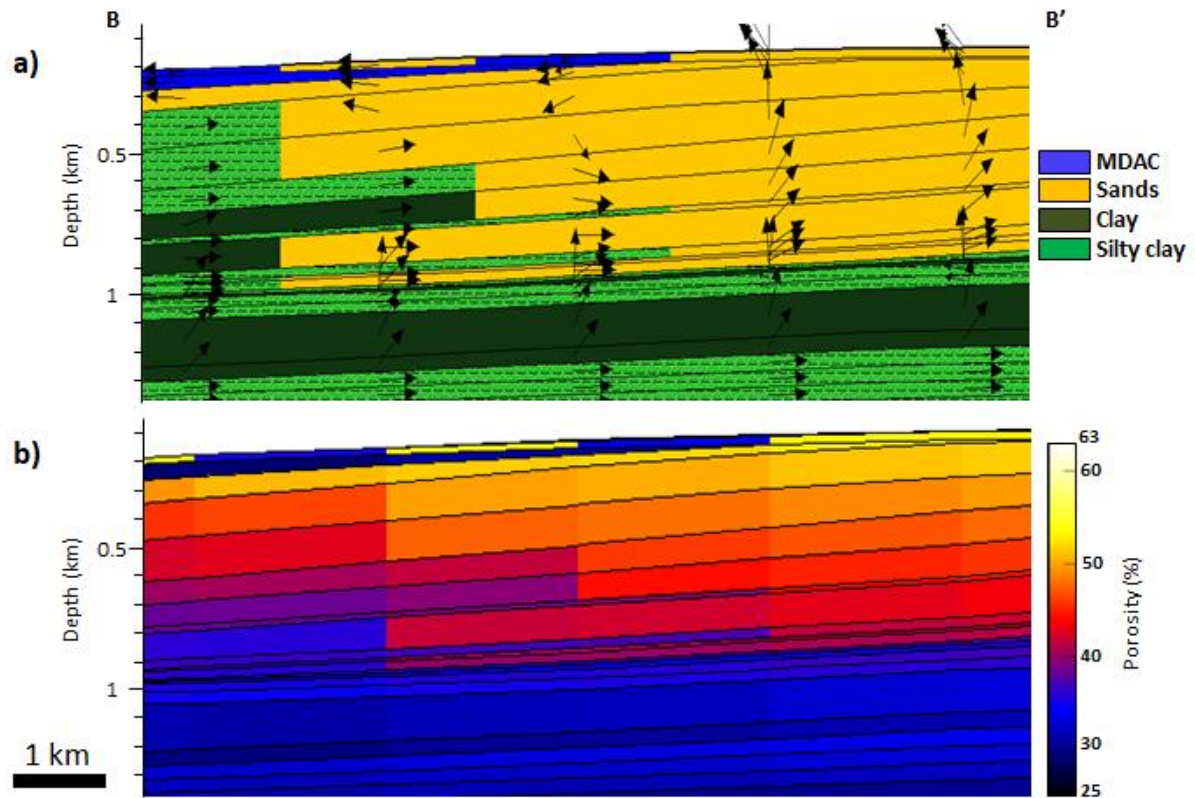
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1271 **Figure 16. Modelled results along the 2D section B-B' shown in Figure 13. a) Facies distribution; b) Porosity (%). The**  
 1272 **black arrows show the water flow direction which is a function of facies and porosity.**

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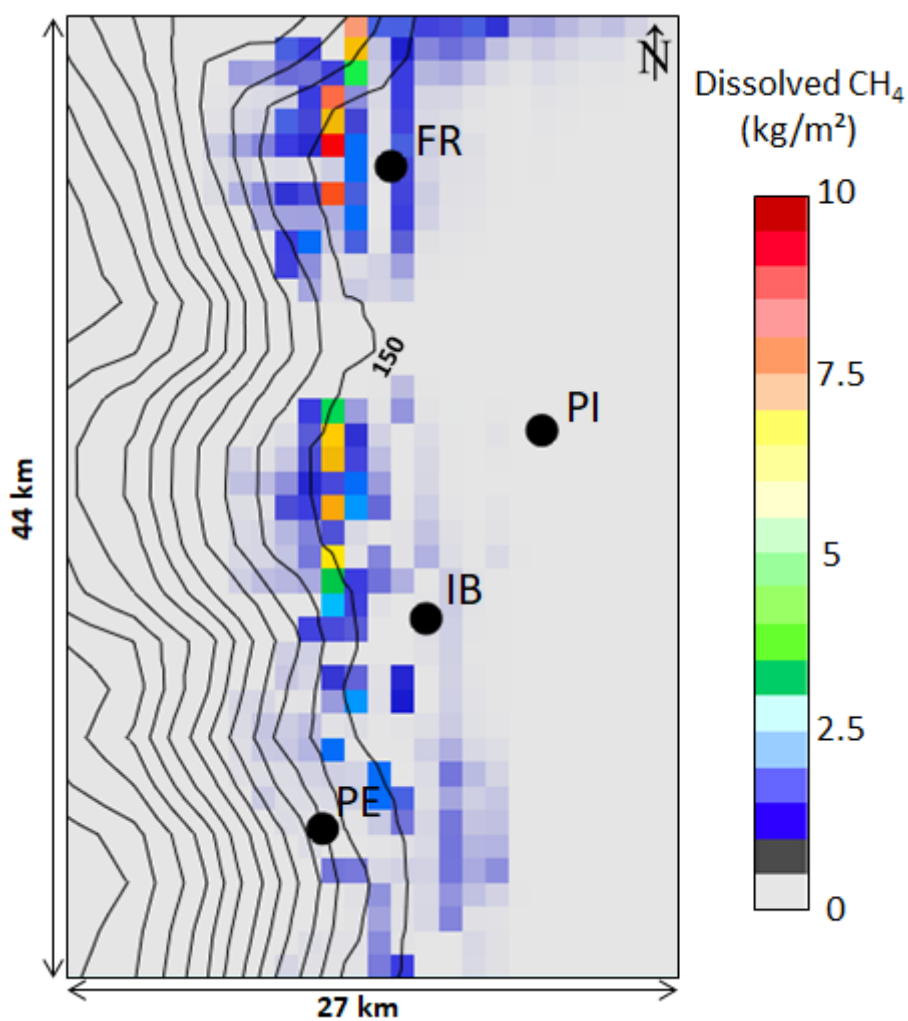
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 1282 **Figure 17. Present-day modelled dissolved methane (kg/m<sup>2</sup>) in the second layer from top seafloor along the northern**  
 1283 **study area emission sites (for map location see Fig. 1b). Black dots indicate the offshorewells (FR – Fregate-1; PI –**  
 1284 **Pingouin-1; IB – Ibis-1; PE – Pelican-1) (Figs. 1, 3). Black lines represent the seafloor bathymetry with a contour**  
 1285 **interval of 50 m.**

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1297 Table 1. Geological layers and sub-layering for the main target area of biogenic gas generation. Interpreted seismic  
 1298 horizons are derived from OROGEN Project (Total) (Basement to Oligocene), Ortiz et al. (2020) (Miocene to Seabed),  
 1299 and Michel (2017) (Plio-Pleistocene units). The two uppermost layers are created by a lithoswitch to account for  
 1300 precipitation of MDACs during CH<sub>4</sub> upward migration.

<b>Top Age (Ma)</b>	<b>Layers</b>	<b>Interpreted Horizons from seismic</b>	<b>Sub-layering</b>
0.0	MDAC		
0.14	Seabed	x	
0.25	Plio-Pleistocene U3	x	8 sub-layers
1.76	Plio-Pleistocene U2	x	7 sub-layers
3.53	Plio-Pleistocene U1	x	
5.30	Miocene	x	6 sub-layers
13.82	Langhian- Serravallian	x	
20.24	Aquitanian		
23.03	Oligocene	x	
33.90	Upper Eocene		
41.20	Lower Eocene		
56.00	Paleocene		
66.00	Upper Cretaceous	x	
100.50	Albian	x	
113.00	Aptian	x	
125.00	Barremian		
130.00	Neocomian		
145.00	Top Jurassic	x	
175.60	Top Lias		
201.30	Top Triassic	x	
250.00	Top Basement	x	

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**Table 2. Range of parameters considered as uncertain in this study (Min and Max) and values selected for an optimal biogenic gas production (“This study”).**

<b>Input Parameter</b>	<b>Min</b>	<b>Max</b>	<b>This Study</b>	<b>Unit</b>
TOClab	20	24	22	%
TOCzlab	15	19	19	%
Rbio	0.16	9	1.7	
Ea	80	110	83	kJ/mol
Sbio	0.2	0.4	0.35	
Salinity	40	60	50	g/L
$\mu(T)$	30	55	32	°C

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1338 **Table 3. Source rock age, modelled temperature and thermal conductivity. TOC bio-refractory (TOC<sub>bio-ref</sub>) values are**  
 1339 **defined after the Rock-Eval analysis (Table S1).**

<b>Source Rock</b>	<b>Top_Age</b>	<b>Mean Depth</b>	<b>Mean Temperature</b>	<b>Mean Thermal Conductivity</b>	<b>TOCbio-ref</b>
	<b>(Ma)</b>	<b>(m)</b>	<b>(°C)</b>	<b>(W/m.°C)</b>	<b>(%)</b>
Plio-Pleis_5	1.76	585	14	1.60	0.49
Plio-Pleis_4	1.98	618	16	1.64	0.42
Plio-Pleis_3	2.20	670	17	1.66	0.44
Plio-Pleis_2	2.42	708	20	1.63	0.30
Plio-Pleis_1	2.87	823	22	1.61	0.29
Miocene	5.53	1100	30	1.54	0.51

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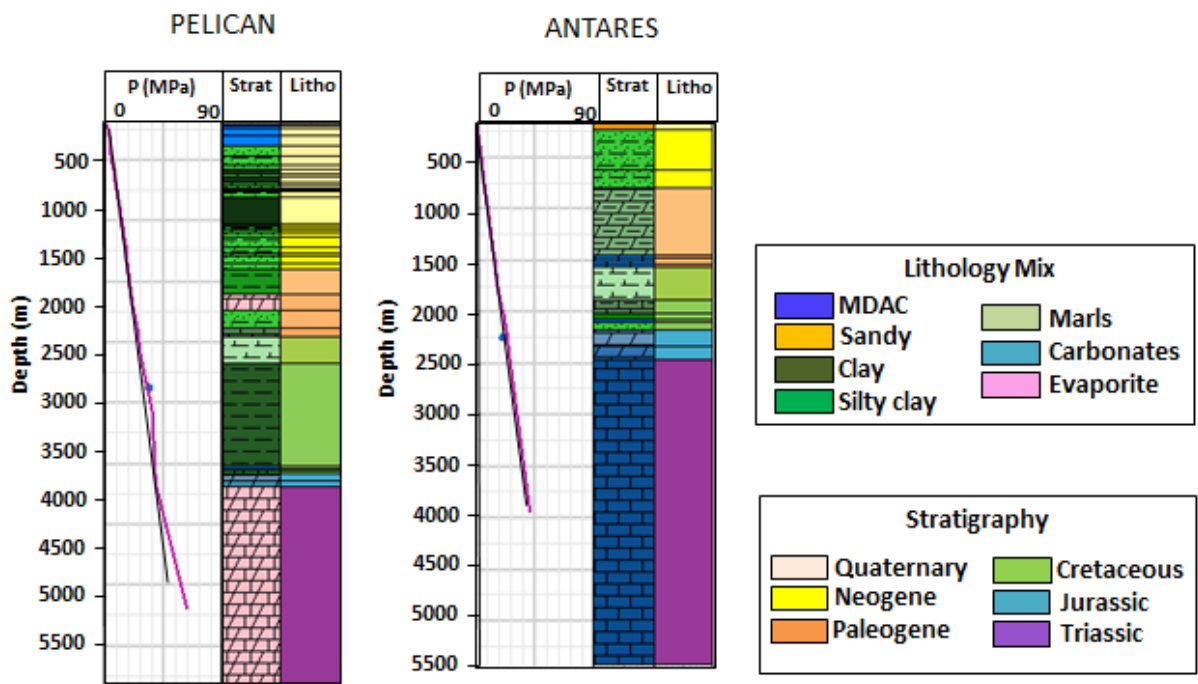
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1361 SUPPLEMENTARY MATERIAL:



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1363 Figure S1. Pressure calibration for two wells. Well location is given in Fig. 3.

1364 Table S1. Rock-Eval results on cuttings collected from two offshore wells (Pingouin-1 and Pelican-1). Well locations  
 1365 are given in Fig. 3.

Sample	Depth m	S2 mgHc/g-rock	Tmax °C	HI mg Hc/g TOC	OI mg CO <sub>2</sub> /g TOC	TOC %
<b>PINGOUIN-1</b>	595	<b>0.22</b>	424	51	286	<b>0.44</b>
<b>PINGOUIN-2</b>	715	<b>0.12</b>	437	41	427	<b>0.28</b>
<b>PINGOUIN-3</b>	735	<b>0.11</b>	423	41	387	<b>0.26</b>
<b>PINGOUIN-4</b>	875	<b>0.04</b>	422	21	501	<b>0.2</b>
<b>PINGOUIN-5</b>	955	<b>0.09</b>	421	31	343	<b>0.29</b>
<b>PINGOUIN-6</b>	1025	<b>0.11</b>	420	39	334	<b>0.29</b>
<b>PINGOUIN-7</b>	1125	<b>0.05</b>	420	25	430	<b>0.22</b>
<b>PINGOUIN-8</b>	1145	<b>0.14</b>	420	39	292	<b>0.35</b>
<b>PINGOUIN-9</b>	1265	<b>0.14</b>	422	43	307	<b>0.32</b>
<b>PINGOUIN-10</b>	1325	<b>0.15</b>	421	47	279	<b>0.32</b>
<b>PINGOUIN-11</b>	1425	<b>0.1</b>	421	33	305	<b>0.31</b>
<b>PELICAN-1</b>	740	<b>0.14</b>	421	32	328	<b>0.44</b>
<b>PELICAN-2</b>	860	<b>0.15</b>	424	34	306	<b>0.44</b>
<b>PELICAN-3</b>	960	<b>0.19</b>	424	38	290	<b>0.49</b>
<b>PELICAN-4</b>	1050	<b>0.19</b>	422	43	292	<b>0.46</b>
<b>PELICAN-5</b>	1200	<b>0.1</b>	422	27	321	<b>0.36</b>
<b>PELICAN-6</b>	1280	<b>0.15</b>	439	36	387	<b>0.41</b>
<b>PELICAN-7</b>	1493	<b>5.67</b>	432	55	106	<b>10.35</b>
<b>PELICAN-8</b>	1500	<b>0.21</b>	421	38	238	<b>0.53</b>
<b>PELICAN-9</b>	1530	<b>0.2</b>	420	43	284	<b>0.47</b>

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