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Viviane Casenave, Aurélien Gay, Patrice Imbert. Spider structures: records of fluid venting from methane hydrates on the Congo continental slope. Bulletin de la Société Géologique de France, 2017, 188 (4), 10.1051/bsgf/2017189. hal-02965041

HAL Id: hal-02965041 https://hal.science/hal-02965041v1

Submitted on 12 Oct 2020

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Spider structures: records of fluid venting from methane 1 hydrates on the Congo continental slope. 2 Les structures en araignée : enregistrement d'échappements 3 de fluide provenant des hydrates de méthane, sur la pente 4 continentale du Congo 5 6 Viviane CASENAVE^{*1-2}, Aurélien GAY^{*1}, Patrice IMBERT^{*2} 7 *¹ Géosciences Montpellier, UMR 5243 – CC 60, Université Montpellier 2, place 8 E. Bataillon, 34095 Montpellier Cedex 05, France 9 *² CSTJF, Total, Avenue Larribau, 64018 Pau Cedex, France 10 11 Corresponding author: Viviane Casenave (viviane casenave@hotmail.com) 12 13 Keywords: Methane seep; methane hydrates; bottom-simulating reflector (BSR); dynamic 14 15 seepage; methane-derived authigenic carbonates (MDAC) Mots-clés : fuite de méthane, hydrates de méthane, BSR (bottom-simulating-reflector), fuite 16 dynamique, carbonates dérivés du méthane (MDAC) 17

18 Abstract

19 Fluid seepage features on the upper continental slope offshore Congo are investigated using 20 multi-disciplinary datasets acquired during several campaigns at sea carried out over the last 15 years. This datasets includes multibeam bathymetry, seismic data, seafloor videos, 21 22 seafloor samples and chemical analyses of both carbonate samples and of the water column. 23 Combined use of these datasets allows the identification of two distinctive associations of 24 pockmark-like seabed venting structures, located in water depths of 600-700 m and directly 25 above a buried structural high containing known hydrocarbon reservoirs. These two features 26 are called spiders due to the association of large sub-circular depressions (the body) with 27 smaller elongate depressions (the legs). Seismic reflection data show that these two 28 structures correspond to amplitude anomalies located ca. 60-100 ms below seabed. The 29 burial of these anomalies is consistent with the base of the methane hydrate stability domain, which leads to interpret them as patches of hydrate-related bottom-simulating 30 reflection (BSR). 31

32 The morphology and seismic character of the two structures clearly contrasts with those of 33 the regional background (Morphotype A). The spider structures are composed of two 34 seafloor morphotypes: Morphotype B and Morphotype C. Morphotype B makes flatbottomed depressions associated with the presence of large bacterial mats without 35 36 evidence of carbonates. Morphotype C is made of elongated depressions associated with the 37 presence of carbonate pavements and a prolific chemosynthetic benthic life. On that basis of 38 these observations combined with geochemical analyses, the spider structures are 39 interpreted to be linked with methane leakage 40 Methane leakage within the spider structures varies from one morphotype to another, with

41 a higher activity within the seafloor of Morphotype C; and a lower activity in the seafloor of

Morphotype B which is interpreted to correspond to a domain of relict fluid leakage. This
change of the seepage activity is due to deeper changes in gas (or methane) migration
corresponding to the progressive upslope migration of fluids. This phenomenon is due to the
local formation of gas hydrates that form a barrier allowing the trapping of free gas below in
the particular context of the wedge of hydrates.

47 Résumé

48 Les caractéristiques des échappements de fluides sur la pente continentale supérieure, au

49 large des côtes du Congo, sont étudiées en utilisant des jeux de données pluridisciplinaires,

50 acquis au cours de plusieurs campagnes marines menées au cours des 15 dernières années.

51 Ces jeux de données comprennent de la bathymétrie multifaisceaux, des données sismiques,

52 des vidéos des fonds marins, des échantillons du fond marin et des analyses chimiques à la

53 fois des échantillons de carbonate et de la colonne d'eau.

54 L'utilisation combinée de ces ensembles de données a permis l'identification sur le fond de 55 l'eau, de deux associations distinctes de structures d'échappements de fluides de type 56 pockmark, localisées entre 600 et 700 m de profondeur d'eau et directement au-dessus d'un 57 haut structural enterré contenant des réservoirs d'hydrocarbures connus. Ces deux 58 structures sont appelées araignées en raison de l'association des grandes dépressions 59 subcirculaires (le corps) avec de petites dépressions allongées (les pattes). Les données de 60 sismique réflexion montrent que ces deux structures correspondent à des anomalies d'amplitude localisées à 60-100 ms en-dessous des fonds marins. L'enfouissement de ces 61 62 anomalies est compatible avec la base de stabilité des hydrates de méthane, ce qui conduit à les interpréter comme des patchs de Bottom-Simulating Reflection (BSR) reliés à la 63 présence d'hydrates. 64

La morphologie et la nature des deux structures contrastent clairement avec celles de du 65 contexte régional (Morphotype A). Ces structures en araignée sont composées de deux 66 67 morphotype du fond marin : le Morphotype B et le Morphotype C. Le Morphotype B 68 constitue des dépressions à fond plat associées à la présence de grands tapis bactériens et 69 sans indice de présence de carbonates en fond de mer. Le Morphotype C est constitué de 70 dépressions allongées associées à la présence de croûtes carbonatées et d'une vie benthique 71 chimio-synthétique prolifique. Sur la base de ces observations, combinées à des analyses 72 géochimiques, les structures en araignée sont interprétées comme étant liées à des fuites 73 de méthane

74 Les fuites de méthane à l'intérieur de ces structures en araignée varient d'un morphotype à 75 l'autre, avec une activité plus importante dans le fond marin du Morphotype C, et une 76 activité plus faible dans le fond marin du Morphotype B, qui est interprété comme étant un 77 vestige de site d'échappement de fluides. Cette évolution de l'activité d'échappement de 78 fluides est due à des changements plus profonds dans la migration du gaz (ou du méthane), correspondant à la migration progressive des fluides vers le haut de la pente. Ce phénomène 79 80 est dû à la formation locale d'hydrates de gaz qui forment une barrière permettant le 81 piégeage sous-jacent de gaz libre, dans le contexte particulier du biseau des hydrates.

82 Introduction

Fluid flow features represent anomalies generated during past and present subsurface flow
of fluids (oil, gas, brine, groundwater and magmatic fluids) from source to the seabed or land
surface [Cartwright *et al.*, 2007; Løseth *et al.*, 2009]. The type of structure generated
depends on a variety of parameters as for instance the source of fluid, the flow type, the
structural setting and the nature of the host sediments [Cartwright *et al.*, 2007; Huuse *et al.*,
2010]. Pockmarks, mud volcanoes, gas hydrates, chimneys, pipes, some sediment injections,

and some carbonate bodies (e.g methane-derived authigenic carbonates, MDAC), and
related diagenetic phenomena are examples of geologic features associated with temporally
varying systems of focused fluid seepage through the seabed [Cartwright *et al.*, 2007; Judd
&Hovland, 2007; Løseth *et al.*, 2009; Huuse *et al.*, 2010].

93 Seafloor fluid flow features, such as pockmarks, are commonly found overlying deep or 94 shallow hydrocarbon reservoirs [Heggland, 1998], and along continental margins where they 95 are often associated with localized gas hydrate accumulations [Bünz & Mienert, 2004; Ivanov 96 et al., 2007]. On 3D seismic data, these geologic features are commonly found to be 97 underlain by columnar zones of attenuated and disrupted reflections called "acoustic 98 chimneys", or "blow-out pipes" [Løseth et al., 2011] depending whether the authors just 99 describe their seismic character or consider them as genuine fluid escape conduits. 100 Fluid flow features specifically related to methane hydrates and their dynamics have 101 received specific attention over the past decade both for their potential role in climate 102 change [Maslin et al., 2010] and their growing economic interest [Milkov & Sassen, 2002].

Accumulation of gas hydrate below the seafloor occurs either as stratiform accumulation
associated with a bottom simulating reflection (BSR) in the subsurface [Shipley *et al.,* 1979]
or as shallow gas hydrates accumulations preferentially localized along fault planes

106 [Simonetti *et al.*, 2013] and below pockmarks [Marcon *et al.*, 2014].

107 The use of high-resolution three-dimensional seismic data brings new insight to the

108 occurrence of gas hydrates, their dynamics of growth and demise, and relationship with

109 venting points and deep plumbing systems. This includes sediment collapse and pockmarks

110 formation due to hydrate dissolution forming specific features called "hydrate pockmarks"

111 [Sultan *et al.*, 2010; Imbert &Ho, 2012; Riboulot *et al.*, 2016]; local hydrate accumulations

below the seabed forming "hydrate pingoes" [Hovland & Svensen, 2006; Sérié et al., 2012]

and hydrate mounds [Matsumoto *et al.*, 2009; Nakajima *et al.*, 2014].

114 The Lower Congo Basin, offshore SW Africa, is a prolific petroleum province that has been 115 extensively explored for more than 30 years, resulting in a growing quantity and quality of 116 exploration data (Séranne, 1999; Marton et al., 2000; Babonneau et al., 2002; Rouby et al., 117 2002; Fort et al., 2004; Broucke et al., 2004; Gay et al., 2006a; Andresen et al., 2011; 118 Beglinger et al., 2012). Numerous studies have recognized the widespread occurrence of 119 past and present fluid flow-related phenomena [Andresen et al., 2011; Gay et al., 2007], 120 including the widespread occurrence of gas hydrates [Cunningham & Lindholm, 2000], 121 pockmarks [Andresen et al., 2011; Gay et al., 2006a] and giant pockmarks that correspond to 122 depressions whose diameter exceeds ca. 1000 m wide, generally found in the deep part of 123 the basin [Marcon et al., 2014; Ondréas et al., 2005; Sahling et al., 2008]. Pockmark 124 commonly seems to be closely linked to gas hydrates occurrence either for some small-scale 125 pockmarks deeply rooted with a BSR [Gay et al., 2006a] or for giant pockmarks showing the 126 presence of gas hydrates in the shallow subsurface [Marcon et al., 2014; Ondréas et al., 127 2005; Sahling et al., 2008].

128 This study presents the discovery, on the upper part of the slope, of a new type of 129 pockmark-like feature corresponding to seafloor fluid vents. These features are called 130 "spider structures" because they combine a subcircular flat-bottomed pockmark ("body" of 131 the spider) with furrows extending upslope over a distance comparable to the diameter of 132 the pockmark ("legs"). This work is based on a highly diverse array of data that allow the 133 well-constrained characterization of the newly defined spider structures. The results provide 134 a potential insight into the processes of seabed fluid venting in the particular context of the 135 pinch out of the BSR. This work aims to propose a genetic model of fluid migration from 136 depth over time in relation to inferred gas hydrate formation near seabed and ongoing methane seepage. The main contribution of this work concerns how seabed vents record 137

138 fluid flux through time, a process of which we still have a limited understanding [*e.g.*

139 Foucher *et al.* 2009].

140 **Geological Setting**

141 The investigated area is located in the Lower Congo Basin, on the Congo slope, between 142 500 m and 1200 m water depth, north of the Congo canyon (Fig.1). The Lower Congo basin is 143 one of many sub-basins along the West African continental margin which was initiated in the 144 early Cretaceous during the opening of the South Atlantic Ocean [Brice et al., 1982; Karner et 145 al., 1997; Marton et al., 2000]. Following the rifting, restricted-marine conditions allowed 146 the deposition of up to 1 km of Aptian evaporites (the Loeme Formation), that constitute the 147 decollement layer responsible for the salt tectonic that characterizes this part of the margin 148 (Fig.2) [Brice et al., 1982; Duval et al., 1992; Liro & Coen, 1995; Lundin, 1992; Valle et al., 149 2001; Uchupi, 1992]. The gravitational sliding of the sedimentary cover above the salt layer 150 defines an upslope extensional domain characterized by rafts and grabens and a downslope 151 compressive domain characterized by salt diapirs, canopies and walls, each domain being 152 about 100 km wide within the Lower Congo Basin [Duval et al., 1992; Fort et al., 2004; 153 Lundin, 1992; Marton et al., 2000; Rouby et al., 2002]. The study area is located in the 154 extensional domain and is structured into horsts and grabens bounded by listric faults 155 (Fig.2).

The stratigraphy of post-rift sediments consists of two major sequences; these are separated by the Oligocene Unconformity that reflects a major change in ocean circulation and climate [Séranne *et al.*, 1992; Séranne, 1999]. The latter sequence corresponds to the icehouse period that began in the early Oligocene. This sequence has been characterized by an overall regression superimposed by alternating dry and wet climate periods and high amplitude (>100m) high frequency (100 kyr) sea level oscillations [Bartek *et al.*, 1991; Miller *et al.*,

2005; Seranne, 1999; Zachos et al., 2001]. During this period, sedimentation has been 162 163 dominated by the progradation of a terrigeneous wedge associated with the deep incision of 164 the Congo submarine canyon [Séranne, 1999]. The large amount of terrigeneous material 165 has led to the formation of the large turbidite systems of the Congo fan [Brice et al., 1982; 166 Broucke et al., 2004; Droz et al., 1996; Uchupi, 1992]. Deep thermogenic fluids [Gay et al., 167 2006a] migrating upward are preferentially trapped in sandy turbidite channel reservoirs. 168 Significant oil and gas discoveries have been made in this basin over the last two decades 169 [Beglinger et al., 2012; Burwood, 1999; Cole et al., 2000]. Since the early Pliocene, the shelf 170 and the slope have been bypassed because of the deep incision of the Congo canyon that 171 directly connects the Congo River with the deep basin and the abyssal plain, down to 4000 m 172 water depth [Babonneau et al., 2002]. As a consequence, the slope, including the study area, 173 has only been receiving sparse amounts of fine-grained sediments along with pelagic 174 production [Jansen et al., 1984; Pufahl et al., 1998; Uenzelmann-Neben, 1998]. 175 The Pliocene-present interval contains widespread fluid escape features, at seabed and in 176 the subsurface, indicating past and ongoing bypass of the regional seal [Andresen et al., 2011; Cartwright, 2011; Gay et al., 2006a], which corresponds to a major polygonal fault 177 178 system [Cartwright, 2011; Gay et al., 2004].

179 Data and Methodology

The dataset (Fig.3) includes multibeam bathymetry, seismic data, seafloor videos, seafloor
samples geochemistry and chemistry of the water column. All these data have been acquired
during several marine campaigns carried out over the last 15 years (Zaiango, 1999; Zairov,
2000, Biozaire, 2001, Total Geohazard, 2011).

184 Seismic data

The study is based on both 3D seismic volumes and 2D, high resolution (HR) seismic profiles. The seismic interpretation and attribute analyses were performed with the SISMAGE software developed by Total [Guillon & Keskes, 2004]. All data are displayed in two-way travel time (TWT) and values are expressed in s (TWT) or ms TWT. The average velocity in the upper section studied here is estimated at ca. 1500 m.s⁻¹ [Sultan *et al.* 2007], so that 100 ms TWT roughly correspond to 75 m.

191

Exploration and High Resolution (HR) 3D seismic data

Two 3D seismic volumes with a multichannel offset, acquired for hydrocarbon exploration 192 193 are used for this study (Fig. 3). The first dataset covers about 1900 km² with a line spacing of 194 12.5 m and a CDP distance of 12.5 m. The dominant frequency is 70 Hz in the upper 100 ms TWT, with a significant frequency content up to 80-90 Hz, giving a vertical resolution of ~ 4 m 195 (at a velocity of 1700 m.s⁻¹) and a horizontal resolution of ca. 20 m; the vertical sampling is 196 197 4 ms TWT. The second dataset is a high-resolution 3D volume covering 120 km² with a line 198 spacing of 6.25 m in both directions (in brown on Fig.3) and a sampling rate of 3 ms TWT. 199 The dominant frequency is 70 Hz in the upper 100 ms TWT (similar to the regional survey), 200 but with a significant frequency content up to 100-110 Hz in the upper 100 ms TWT of the sedimentary pile; this gives a vertical resolution of ca. 3 m for a velocity of 1700 m.s⁻¹. The 201 202 seabed signal is not symmetrical, which means that the data are not zero-phase [Brown, 203 2011]. This study mainly used the amplitude, "dip" and coherence [Bahorich & Farmer, 204 1995] attributes. The coherency attribute estimates over a window selected by the interpreter the correlation between a seismic trace and the adjacent ones. The "dip" 205 206 attribute is an approximation of the local slope gradient in degrees; it was calculated here at 207 each sample over the 8 surrounding points.

208

High resolution 2D-AUV seismic data

209 High-frequency 2D seismic data with high resolution (HR) and low penetration (2D-AUV and 210 Chirp for example) are generally used to study sub-seafloor anomalies [Orange et al., 1999; Savini *et al.*, 2009]. All AUV data were acquired using C&C's **C-Surveyor** I[™]. 211 212 Roughly 300 km of High Resolution (HR) 2D-AUV seismic profiles were used for the study 213 (Fig.3). The AUV was equipped with an Edge Tech Chirp Subbottom Profiler. The transmit 214 pulses are generated in the frequency band between 2 and 8 kHz. The high-resolution 2D-215 AUV seismic profiles have a spacing of 175 m in a SW-NE direction and about 1000 m in the 216 orthogonal direction over the area of interest. The signal has a penetration of about 100 ms 217 TWT and a resolution of 6-10 cm. Due to the low penetration of the high frequency signal, 218 no reflections were identified below around 70 m below the seafloor. These 2D seismic 219 profiles were interpreted using a combination of the recorded amplitude and its "envelope", 220 a moving Root Mean Square (RMS) average.

221

1 Seabed bathymetry

Bathymetry data were acquired by the AUV equipped with a Simrad EM 2000 Swath bathymetry system collecting soundings in a 200-meter swath underneath. Multibeam data were processed at a 3-meter bin size using C&C's proprietary HydroMap software and the depth values are referenced to Lowest Astronomical Tide (LAT). Bathymetry data cover an area of about 400 km² (Fig. 3) with a horizontal resolution of about 3 m. The vertical resolution provided by the 200 kHz source is a few cm.

228 Side

Side-Scan Sonar (SSS) data:

Side-Scan sonar data were collected by the AUV equipped with a dual frequency chirp Edge
Tech Side Scan Sonar. It uses a calibrated wide band digital frequency modulated (FM) signal
to provide high resolution, low-noise images. This sonar simultaneously transmits linearly

swept FM pulses centered at two discrete frequencies: 120 kHz and 410 kHz with a
maximum cross-track resolution of respectively 6.25 cm and 1.8 cm. The acoustic
penetration can reach several meters depending on the sediments at the sea bottom. The
backscatter data are used for the impedance contrast detection in the seafloor sediments
and in the shallow sub-seafloor. High backscatter intensity is displayed in dark tones (Fig.3).

237

Seafloor videos and sampling:

Two video transects were acquired during two surveys (Fig.3). The first one (ROV track 1)

corresponds to the ZAIANGO IFREMER/TOTAL-FINA-ELF program (Zairov mission in 2000)

240 with the "ROV Victor" (Remote Operated Vehicle). The second one (ROV track 2)

241 corresponds to an industrial geotechnical campaign acquired by SEAROV in 2012 for Total

with the "ROV Seaeye Panther". The last ROV dive has allowed collecting pictures of the

seafloor that have never been published yet. The ROV dives were partly dedicated to the

sampling of massive carbonate crusts by video-controlled grab on 2 different sites (Fig.3).

245 **Isotopic analyses:**

246 Isotope values of carbon and oxygen were obtained by with the Isotope-Ratio Mass Spectrometry (IRMS) method by the use of a Delta V+ spectrometer after extraction of the 247 CO₂. Analytic precision of measurements is 0.1 ‰ for both δ^{18} O and δ^{13} C values. The 248 isotopic ratio of carbon represents the difference between the ${}^{13}C / {}^{12}C$ values (Table 1) 249 250 measured on a sample relative to the Pee Dee Belemnite (PDB) international standard. The isotopic ratio of oxygen indicates the difference between the 18 O / 16 O ratio (Table 1) 251 252 measured on a sample and an international standard corresponding to the SMOW (Standard 253 Mean Ocean Water).

254

Water column chemistry:

255	During the Zairov mission in 2000, water was sampled in several pressurized bottles, in both
256	hydrocasts and ROV sampling, to measure the actual concentrations of dissolved methane
257	and also the concentrations of iron, manganese end silicon dissolved.
258	Hydrocasts were also carried out using a SBE 9/11+ Seabird conductivity-temperature-
259	depth (CTD) sensor with a Wet Labs nephelometer, at the BZR-01 Station (see Fig.3.B for
260	location). This CTD/rosette was also equipped with 16 pressurized bottles of 8 l capacity in
261	order to sample the water column.
262	In addition, a Victor ROV dive was carried out above the area of interest, between 550 m to
263	800 m water depth, in which 15 pressurized minibottles of water were sampled, 3 m above
264	the seabed (Fig.3.B). Aliquots of 125 ml were immediately collected in glass bulbs with
265	Teflon stopcocks and analyzed on board using a chromatographic purge/trap technique
266	[Charlou & Donval, 1993; Charlou et al., 1998]. Aliquots of 60 ml were acidified for Fe and
267	Mn analysis.

268 Geophysical characterization

269 Morphology and distribution of seafloor morphotypes

270 In the Lower Congo Basin, multibeam data were combined with coherency maps derived

- 271 from 3D seismic data in order to better characterize the seafloor morphology. Two
- kilometric scale anomalies were identified at about 600-700 m water depth (Fig.4). Three
- 273 main seafloor morphotypes have been identified:
- 274 <u>Morphotype A</u>: The bathymetric and the slope gradient maps only show slight variations of
- slope angles (Fig. 4A&B). The seafloor is smooth and only a few depressions and mounds are
- visible in the north-western part. The backscatter reflectivity has an average low value

277 displayed as a light grey on Fig.4.C. The coherency is high and shows no major variations 278 over the area (Fig.4.D). This morphotype is considered as the background regional seafloor. 279 Morphotype B: The bathymetric and the gradient maps show two sub-circular flat-bottomed 280 depressions on the seafloor (Fig.4.A&B). They are 2-3 m meters deep on average and are 281 characterized by a rough bottom surrounded by continuous edges. They are both elliptical in 282 shape and their preferential elongation is close to the gradient of the regional NNW-SSE 283 slope. The northwestern depression is approximately 1.5 km long and 1 km wide, 284 representing an area of about 1.2 km². The southeastern depression is about 0.7 km long 285 and 0.6 km wide covering a surface of 0.4 km². Within the flat depressions the backscatter 286 reflectivity is low (Fig.4.C) and the coherency is generally medium (Fig.4.D). A few lower 287 coherency anomalies are also visible on the coherency map. They appear as isolated 288 irregular to crescent-shaped patches, a few tens of meters in length (Fig.4.D). 289 Morphotype C: The bathymetric map shows a set of elongated depressions, about 10-290 m deep (Fig.4.A). They have steep edges with slope angles reaching 35° as shown by Fig.4.B. 291 Nearly 75 % of these elongated depressions trend in a NNW-SSE direction, subparallel to the 292 regional slope gradient. They are very narrow: about 50 m wide for a length ranging from 50 293 m to 1000 m. Some of the elongated depressions widen into elliptical patches, 200 m long 294 and 100 m wide (Fig.4.A). The backscatter map shows high reflectivity anomalies on the 295 seafloor (Fig.4.C), including a few thin and elongated depressions and six of the broader 296 anomalies corresponding to the elliptical patches described on the slope gradient map 297 (Fig.4.C). Within this Morphotype C, all depressions are very low in coherency (Fig.4.D). 298 Morphotypes B and C are associated in two sets, each comprised of a patch of Morphotype 299 B from whose periphery appear to emanate furrows of Morphotype C. In each set, the 300 distribution of the furrows is strongly skewed towards the SE side of Morphotype B, with the 301 orientation of individual furrows ranging from radial (with respect to Morphotype B) to

southeastwards trending, the latter being dominant. For each set, the network of
Morphotype C furrows reaches about one diameter of the patch of Morphotype B in a SE
direction.

305 This association of Morphotypes B and C allows defining two main objects on the seafloor: 306 the deeper one is 2.7 km long and 2 km wide and consists of a large patch of Morphotype B, 307 with peripheral furrows of Morphotype C extending southeastwards; shallower on the slope, 308 a similar feature covers 1.2 km in length and 0.7 km in width and also shows furrows 309 developing upslope from a patch of Morphotype B. They are both called "Spider Structures" 310 (SS) as they consist of a main "body" (i.e. sub-circular patch of Morphotype B) and peripheral 311 "legs" (i.e. elongated Morphotype C). The "Spider Structures" are named SS1 (larger feature) 312 and SS2 (smaller) (Fig. 5).

313 Large amplitude anomalies on seismic sections

The studied seismic interval shows several amplitude anomalies located just underneath the two spider structures previously identified (Fig.6). Two strong amplitude anomalies identified at 1100 ms TWT below seafloor (Fig.6.C) correspond to Miocene turbidite channels that have been exploited for over a decade. They are cut by listric normal faults that compartmentalize the reservoirs. Some of these faults reach the seafloor where they are expressed as curved depressions (Fig.6.A).

Two flat high-amplitude anomalies are also identified in the shallow subsurface just below the two spider structures (Fig.6). Although the used seismic dataset is not zero-phase, the flat reflections can be seen to have a polarity (white/black) opposite to that of the seafloor (black/white) (Fig.6.C.D). These anomalies are almost parallel to the seafloor, slightly converging upslope towards it; in those respects, they fulfill the criteria of BSRs (Bottom

325 Simulating Reflections) and can thus be suspected to correspond to the Base of the Gas
326 Hydrate Stability Zone (BGHSZ) [e.g. Dillon *et al.*, 1980].

327 In order to test this interpretation, 5 couples of temperature/pressures have been estimated 328 along the amplitude anomalies on the basis of their depth of occurrence (pressure) and 329 geothermal gradient (temperature). Three gradients were used, based on the three 330 measurements reported in the vicinity [Sultan et al., 2004]: 48 °C/km, 50 °C/km and 331 56 °C/km. The seabed temperature was estimated as the seabed intercept of Sultan et al.'s 332 dataset at about 6.5 °C. The pressure was taken as hydrostatic, in accordance to what is 333 normally observed at shallow depths with normal sedimentation rates [Osborne & 334 Swarbrick, 1997]. Time-depth conversion was carried out using a compressional acoustic 335 velocity (V_p) of 1500 m.s-1 in these very shallow, uncompacted and unlithified lithologies, as 336 measured in previous studies [Sultan et al., 2007]. Figure 7 shows the comparison between 337 the five (P, T°) points estimated along the suspected BSR and hydrate stability curves for 338 variable methane / ethane mixes, from 100 % to 90 % CH4, as reported in [Sloan & Koh, 339 2007]. There is a good consistency between the burial of the observed reflection and the 340 base of the hydrate stability zone calculated using the locally measured [Sultan et al. 2004] 341 for a gas mixture that contains more than 99 % methane. Other combinations like a gas 342 more enriched in C2H6 (more stable) and a higher geotherm (pushing the stability domain 343 upward) could give the same result, but such solutions seem too speculative to be retained 344 in the absence of representative analyses of the gas at BSR level.

These two patches of BSRs are not strictly parallel to the seabed (Fig.6.C&D) but slightly oblique to it, with a depth below the seabed decreasing from 100 to 60 ms TWT in an upslope direction as the seabed shoals from 700 to 600 m water depth (Fig.6.B). Bottomsimulating reflections normally wedge upslope as they approach the wedge of gas hydrates, thereby reducing the thickness of the gas hydrate stability domain [Field & Kvenvolden, 350 1985]. The tilting of the interpreted BSRs is consistent with the fact that the upslope wedge 351 of gas hydrates is estimated to be located at a water depth around 550 m in the study area 352 [Sultan et al., 2004]. On a map view, the high amplitude anomalies form two patches of 353 BSRs, one covering about 2 km² and the other ca. 0.5 km² (Fig.6.B)). The wider patch of BSR 354 is located in an area where two faults are connected (Fig.6.A). Both BSR patches are 355 associated with an underlying high amplitude chaotic and discontinuous zone, a few ms to 356 150 ms TWT thick (Fig.6.c&D). Such anomalies are commonly interpreted as free gas zones 357 below the BSR [Berndt et al., 2004; Bouriak et al., 2000], as the BSR commonly marks the 358 transition between gas hydrate-bearing sediments and the underlying free gas zone [e.g. 359 Dillon et al., 1980]. The dimming of seismic reflections forms two columns of about 1500 ms 360 TWT high and 600 m wide that extend down to the underlying hydrocarbon reservoirs.

361

Shallow sub-seafloor amplitude anomalies

362 In the study area, 2D-AUV profiles were used to highlight subsurface anomalies in the first 363 70 m below seafloor. The 2D-AUV seismic profile CD crosses the main body of Spider 364 Structure 1 from NE to SW (Fig. 8.A; see Fig. 4 for location). The envelope attribute displays 365 high-amplitude seismic anomalies as dark grey patches. Four levels of irregular high-366 amplitude anomalies were identified in the subsurface right below the main flat-bottom 367 depression of Morphotype B. On both sides of the depression the envelope attribute shows 368 low amplitude parallel and continuous reflections. They correspond to the background 369 seismic Morphotype A in the area, as evidenced on all other 2D-AUV seismic profiles (see 370 Fig. 3 for location).

The two deepest levels, level 1 (60 ms TWT below seafloor) and level 2 (35 ms TWT below seafloor), consist of high-amplitude reflections rather discontinuous, that concentrate under the SW part of Morphotype B (Fig. 8.A). On the contrary, the two shallowest levels, level 3

(25 ms TWT below seafloor) and level 4 (10 ms TWT below seafloor), are present under the
whole depression of Morphotype B (Fig. 8.A.B). In contrast with deeper levels, "Level 4"
rather appears as an interval, 8 to 12 ms TWT thick, composed of closely spaced amplitude
anomalies 30 to 100 m wide each (Fig.8.B).

378 Figure 8.-C illustrates on a 2D-AUV seismic profile (amplitude display) the relationships 379 between reflections outside the anomalies and inside the patch of Morphotype B. 380 Reflections visible laterally to the depression can be followed below the margin before they 381 fade out. They consistently plunge down slightly towards the center of the depression. This 382 combination of downwarping and progressive loss of amplitude may at first glance evoke 383 diffraction hyperbolae at the edge of background reflections. However, real diffraction 384 hyperbolae are clearly expressed around the main anomalies of level 4 for instance, and 385 have a much steeper slope than the gentle downwarping at issue here. This downwarping can be followed at least down to below level 2 on the SW side of the seismic profile shown in 386 387 Fig.8.B. The shape of the crest (in particular the location of the highest point) differs from 388 one horizon to the other, as shown on Fig.8.C. This phenomenon indicates that the down-389 bending is not a seismic artifact but corresponds to a real geological feature.

390 Figure 9 shows 2D-AUV seismic profile EF (see Fig.4 for location). This profile is parallel to profile CD, and partly crosses Morphotype C. The dominant seismic facies is parallel and 391 392 continuous [Mitchum et al., 1977]. The seafloor shows 4 depressions, 5 to 8 ms TWT deep (i.e. 3 to 6 m with a water velocity of 1500 m.s^{-1}) and 50 to 120 m wide along the section; 393 394 they are numbered 1 to 4 from SW to NE on Fig.9. Patches of high-amplitude anomalies 395 develop beneath the depressions. Anomalies 1, 2, 3 and 4 are buried at about 6, 20, 4 and 396 5 ms TWT respectively below the corresponding depressions. They are all associated with an 397 underlying acoustic mask that forms a very steep inverted V-shaped dimming structure. The 398 seismic reflections are disrupted on both sides of the acoustic mask or they are dimmed and

shifted downward suggesting a pull-down effect. The outline of the 2D-AUV profile EF is
shown by a dotted rectangle (Fig.9.A) on a profile extracted from the 3D cube along the
same line. It shows that shallow buried anomalies beneath elongated depressions
(Morphotype C) are all located above the BSR that lies about 90 ms TWT below seafloor
(Fig.6.D).

404 **Biological and geological characterization at the seafloor**

405

Visual identification of seafloor morphotypes

On the slope of the Lower Congo Basin, two ROV dives were used to investigate Spider
Structures 1 and 2 located between 600 m and 700 m water depth. In particular, the ROV
tracks crossed both the body (Morphotype B) and the legs (Morphotype C) of SS1 (see ROV
tracks on Fig.3 for location) without observing any gas bubbles escaping from the seafloor.
Three sites were selected for representative pictures within SS 1 (see Fig.3 for location): Site
1 in the flat-bottomed depression corresponding to Morphotype B, and sites 2 and 3 in the
elongated depressions corresponding to Morphotype C.

413 Morphotype B: Within the flat-bottomed depression, pictures obtained during ROV dives on 414 site 1 (see Fig.3 for location) revealed the presence of white bacterial mats overlying blackish 415 reduced sediments (Fig.10.A). Bacterial mats are discontinuous and consist of several closely 416 spaced patches ranging in size from tens of square centimeters to tens of square meters 417 (Fig.10.A). Bacterial mats are associated with the presence of mostly empty shells of bivalves 418 belonging to the thiotrophic family Vesicomyidae [Ondréas et al., 2005] scattered all over 419 the seafloor (Fig.10.A). Bivalve shells are sometimes grouped together in the periphery of 420 the bacterial mats forming accumulations of empty shells (Fig.10.B) and sometimes 421 associated with living bivalves.

422 Morphotype C: Within elongated depressions, ROV dives on sites 2 and 3 (see Fig.3 for 423 location) revealed the occurrence of outcropping carbonates, with a variable degree of 424 cementation (Fig.10.C, D, E and F). Carbonate outcrops can form tubular and/or nodular 425 rocks partially or totally buried in the sediment which sparingly outcrop on the seafloor 426 forming domes (Fig.10.C). Carbonate can also outcrop as thicker tabular carbonate 427 pavements with a flat top (Fig.10.D&E). These carbonate crusts form massive slabs that are 428 often tilted (Fig.10.E) and even fractured (Fig.10.D). The tilted crusts are a few cm to a few m 429 in thickness. They cover an area of about a few hundred square meters. The white bacterial 430 mats grew up directly on the carbonate pavements forming small and discontinuous patches 431 (Fig.10.D, E, F), and they can be associated with black reduced sediments at the toe of carbonate pavements (Fig.10.F). An abundant benthic life, such as tubeworms, anemones, 432 433 Galathea and bivalves, has been identified on and around carbonate crusts as these provide 434 a solid substrate to which sessile organisms can fix (Fig. 10.E). Living bivalves and empty 435 shells are scattered all over the seafloor of this area.

436

Morphology of seafloor carbonates

437 During the ROV dives, two main types of carbonate were sampled at sites 2 and 3 (see Fig. 3 438 for location): 1) Carbonate pavements, associated with bivalve shells, are the most common 439 (Fig.11.D&E). They consist of very poorly sorted shell fragments that are slightly cemented 440 together. These carbonate rocks have a high porosity and are quite brittle due to the low 441 amount of cement (Fig.11.A&C); 2) Nodular or tubular carbonates, which are less observed 442 as they are often found buried within the sediment (Fig.10.C). The only tube-shaped 443 carbonate recovered has a central conduit about 1 cm in diameter (Fig.11.B) connected to smaller secondary conduits of variable diameter which appear as small holes along the main 444 445 tube (Fig.11.D). Nodules and pipes are much indurated and form hard carbonates.

446

Chemical analyses of carbonates and water samples

Seafloor carbonates isotopic compositions 447

448 The isotopic composition of carbon and oxygen were analyzed on four samples taken from seafloor sites 2 and 3 in patches of Morphotype C (see Fig.3 for location). Delta ¹⁸O and δ^{13} C 449 450 measurements for both sites are displayed on Table 1. The analyses on site 2 were made 451 separately on the cement part and the shell part of the carbonate samples visible on 452 Fig.11.A, and on a bivalve shell taken from the seafloor. The measurement on site 3 was 453 carried out on a carbonate sample visible on Fig.11.C. With negative values of δ 13C (-35.5 ‰ on Site 2 and -34.3 ‰ on Site 3 (Table 1), the carbon isotopic compositions on the 454 455 carbonate cement fraction are nearly the same at both sites. However, the carbon isotopic 456 compositions for the shell fraction of the carbonate sample (Fig.11.A) and for the isolated shell (both at site 2) show a major change, -3.1 % and 2.1 % respectively (Table 1). The δ^{18} O 457 458 values for bulk carbonate fractions are in the range of +3.6‰ to +4.1 ‰ for sites 2 and 3 459 (Table 1).

460

Near-bottom water chemical analysis

During the ROV dive near-bottom waters were regularly collected 1-2 m above the seafloor 461 462 from the northwest corner to the southeast corner of the studied area (Fig.12.A). The water 463 samples were then analyzed for dissolved methane (CH₄), iron (Fe), manganese (Mn) and 464 silicon (Si). Measurements 1-2 (about 820 m water depth) and 13-15 (about 550 m water depth) were made 2 km away from the seafloor anomalies. They were sampled over 465 466 Morphotype A corresponding to the normal background seafloor. Except for point 2, measurements 1, 13, 14 and 15 range from 3 to 6 nmol/l for CH₄, 153,7 to 308,7 nmol/l for 467 468 Fe, 9 to 16,9 nmol/l for Mn and 22,3 to 31,7 µmol/l for Si (Fig. 12.A and refer to Table 2-B 469 for exact values).

470 The only measurement made over Morphotype Bat point 3 (Table 2-B) yieleded a CH₄

471 concentration of 16 nmol/l. Over Morphotype C, CH₄ concentration is higher with an

472 average of 38 nmol/l and reached four times higher values at points 5 and 6 (Table 2-B).

473 Dissolved methane concentrations measured over the Morphotype C of the deeper Spider

474 Structure 1 (samples 4, 5, 6, 7 and 8) are higher than those measured over the Morphotype

475 C of the shallower spider structure 2 (samples 10, 11 and 12) (Fig.12.A, Table 2-B).

476 Fe and Mn values measured over both Morphotype B and C are comparable to those over

477 Morphotype A (Table2-B), with the exception of a single sample (point 8).

478 Calibration values are given by silica due to its low solubility in water. With values ranging

479 from 22,3 to 39,1 μmol/l and a slight decrease with water depth, silica concentrations are

480 consistent with dissolved ratios in seawater [Cheong *et al.,* 2014].

481 Water column chemical analysis

482 Complementary analyses have been conducted during the cruise. A vertical CTD/rosette was

483 operated in the water column over the seafloor anomaly (See Fig.3.B for location). The

484 deepest measurement is very close to point 5 measured over the seafloor during the ROV

dive. The dissolved methane concentration decreases downward reaching a minimum value

486 of 0.7 nmol/l at 540 m water depth (100 m above the seafloor). From this depth and

487 downward the dissolved CH₄ shows a regular increase reaching its highest value of 4.1

488 nmol/l at 646 m water depth, close to the seafloor (Fig.12.C and Table 2-A).

489 The Fe and Mn vertical profiles show a slight increase down to about 540 m water depth

490 (Fig.12.B and Table 2-A). From this depth downward the Fe and Mn concentrations increase

491 more rapidly reaching the values of 75,1 nmol/l and 6,4 nmol/l respectively at 653 m water

492 depth, close to the seafloor (Fig.12.B).

493 **Discussion**

494 Spider structures are made of a central depression forming a giant pockmark (Morphotype 495 B) bordered by elongated depressions (Morphotype C) extending dominantly upslope. Flat-496 bottomed giant pockmarks reminiscent of Morphotype B have been reported in literature 497 from the deeper parts of the Lower Congo Basin [e.g Ondréas et al. 2005] and the Western 498 Mediterranean Sea [Ingrassia et al., 2015]. The set of hydrate pockmarks reported by Sultan 499 et al., 2014 in the deep Niger Delta are also flat-bottomed and exceed 500 m in diameter, 500 making them quite similar to the other examples, although they were not formally referred 501 to as "giant" by the authors. These pockmarks appear as isolated fluid flow features in associations of giant pockmarks with peripheral elongated depressions and have not been 502 503 described yet. However a close look at Figure 1 of Marcon et al. (2014) shows 3 or 4 short 504 (ca. 100-m-long) high-reflectivity furrows extending upslope of the giant Regab pockmark, 505 but these are quite inconspicuous and have not been described as such by the authors. They 506 might be seen as "short-legged spider structures" by reference to the example shown here.

507 In addition, the Spider Structures develop right above the structural culmination of a proven 508 hydrocarbon reservoir, and are underlain by a seismic reflection that has all the 509 characteristics of a hydrate BSR. Those three factors: 1) surface geometry analogue to that 510 of hydrate pockmarks; 2) presence of a BSR underneath and 3) structural setting over a 511 hydrocarbon field strongly suggest that the two observed Spider Structures could result from 512 dysmigration of hydrocarbons from the underlying reservoir. The following discussion will 513 challenge this hypothesis, starting from water column and seabed data and moving 514 progressively down. The following issues will be addressed: do spiders reflect present 515 seepage? The provenance of the fluids and the migration pathways will be discussed as well 516 as the temporal variability and the origin of the pockmark depression. Finally, the resulting

517 interpretation will be developed into a full genetic and evolutionary model of the Spider518 Structures.

519

Are Spider Structures seafloor seeps?

520 Fluid venting activity within the spider structures

Background dissolved methane concentrations in the deep ocean are normally below 0.9
nmol/l [Scranton & Brewer, 1978]. Significantly higher values just above seafloor or in the
water column are considered indicative of significant fluid expulsion [Gay *et al.*, 2006b;
Sassen *et al.*, 1994, 2001; Suess *et al.*, 1999].

In the study area, three values of methane concentrations were measured away from the two venting sites, two at 3 nmol/l and one at 6 nmol/l. This is higher than values normally found as ocean background [Scranton & Brewer, 1978]. This could be due to the proximity of active sites of gas release and the presence of an active hydrocarbon generating system in the area.

530 The values observed above Spider Structure 1 (SS 1) and 2 (SS2) are comprised between 16 531 and 70 nmol/l. This is about 10 to 80 times the upper limit of normal marine background 532 values, and still 4 to 18 times the average value of the local background; however, these 533 values remain about 3 orders of magnitude below the saturation value for the local 534 thermodynamic conditions (ca. 60,000 nmol/l, http://models.kl-edi.ac.cn/models/ch4-sea, 535 from [Duan & Mao, 2006], accessed 2016/06/21). These values indicate an actual anomaly of 536 methane on both spider structures, albeit with a moderate flux, which is consistent with the 537 fact that no gas bubbles release was observed at the seafloor. Such methane concentrations 538 are not as large as those typically found in sites of gas venting, in particular in other parts of the Lower Congo basin [e.g. Ondréas et al., 2005]. These relatively low methane 539 540 concentrations measured over Morphotype B and C could be due to a progressive release of

541 methane by steady dissolution of BSR hydrates, which are known to act as dynamic systems
542 [Sultan *et al.*, 2014].

Let us now examine the differences between the two spider structures: eight values of CH4 concentration were recorded for Morphotype C, five of them over Spider Structure 1 (SS1) and three over SS2. The two sets are well contrasted, with an average of 50 nmol/l for SS1 and 20 nmol/l for SS2, in each case with pretty well clustered values. This strongly suggests that SS1 is currently more active than SS2.

It is then possible to examine the variability between the two Morphotypes: as mentioned
above, only one single value was obtained for Morphotype B, in SS1, at 16 nmol/l. This single
value is three times smaller than the average recorded over Morphotype C in the same SS1.

551 In order to better assess the significance of this contrast, we compared the ROV

observations made on Morphotypes B and C. Measurements of CH4 concentrations capture

one moment in time, and it is known that venting is an episodic phenomenon [Tryon et al.,

1999]. On the contrary, sustaining benthic life requires steady supply of nutrients (methane

for chemosynthetic communities). The observation at the seafloor of bacterial mats in

556 Morphotype B, and an active benthic life combined with carbonate pavements in

557 Morphotype C indicates sustained gas venting at both sites.

558 One hydrocast collected water samples above Morphotype C at various water depths 559 (Fig.12). Dissolved methane decreases regularly upward from the lowest measurement up to 560 ca. 550 m, which is interpreted to reflect the presence of a methane plume undergoing 561 progressive dilution upwards. The lower 2 measurements have CH4 concentrations of ca. 4 562 nmol/l, about 9 times what is considered as the upper limit normal oceanic background 563 [Scranton & Brewer, 1978]. Above 550 m, the values steadily increase upwards, a classical 564 behavior in surface waters as methane is a product of metabolism in the intestinal tract of

565 zooplankton and fish [Dafner et al., 1998; Lamontagne et al., 1973; Oremland, 1979]. The 566 hydrocast also recorded iron and manganese concentrations, which are well correlated with 567 CH4 in the lower part influenced by the plume. On board ROV measurements, 1-2 m above 568 the seafloor, showed localized peaks of dissolved methane concentrations above both 569 Morphotype B and C; this indicates that localized points of emission may be active 570 simultaneously in both morphotypes; however methane venting is much more active over 571 Morphotype C rather than over Morphotype B. The seepage sites have thus fed distinct 572 methane plumes all contributing to a much larger plume identified in the water column 573 using the hydrocast.

574 Although Fe and Mn concentrations seem to be correlated with methane venting in the 575 hydrocast record, they do not show significant correlation with the dissolved methane 576 concentration at the seafloor over Morphotypes B and C. The rapid oxidation of iron in the 577 water column can explain the fact that iron concentrations at dissolved methane emission 578 points are sometimes close to the ocean background, suggesting that such gas vents have a 579 variable and maybe a lower activity. On the contrary, the high iron concentrations could 580 correspond to an active gas plume with a steady flow. The in situ production/oxidation of 581 methane can be coupled to the cycling of Mn [Sujith et al., 2014]. The high concentration of 582 Mn in pore water probably suggests the participation of subsurface microorganisms in the 583 geochemical cycling of diverse substrates and their active involvement in the release of Mn 584 [Lovley, 1991]. It could also be attributed to the slower rate of oxidation compared to that of 585 reduction in anoxic sediments [Yadav, 1996]. Dissolved CH₄-Fe-Mn anomalies are the result 586 of fluid seepage into the water column forming a 110-m plume (Fig.12.B.C).

Based on the chemical analyses in bottom seawater and in the water column (hydrocasts),
Spider Structures 1 and 2 can be considered as large seafloor seeps resulting from the
clustering of u numerous smaller seepage sites, as shown for the Haakon Mosby Mud

Volcano [Milkov *et al.*, 2004; Vogt *et al.*, 1997], in the Barents Sea [Lammers *et al.*, 1995], on
the Cascadia Margin [Suess *et al.*, 1999] and in the Lower Congo Basin [Charlou *et al.*, 2003;
Gay *et al.*, 2006b].

593

Flux vs. carbonate development

594 Having established that the Spider Structures are sites of methane seepage, we will now 595 address the issue of the spatial variability of methane flux, based both on the measured 596 concentrations that reflect instantaneous flux and on the absence / presence / type of benthic communities of seep carbonates, which both inform on the mid-term flux. 597 598 First and foremost, in what conditions can methane seep up to the seabed? In normal 599 subseafloor conditions without external input of dissolved methane, the sediment pile 600 shows a bacterial zonation in which bacteria live on less and less energetically efficient redox 601 pairs with increasing depth below seabed. The deepest zone corresponds to 602 methanogenesis, while the one just above is the sulfate reduction zone. Dissolved methane 603 generated by microbial activity is typically consumed within sediment by anaerobic oxidation 604 coupled with reduction of sulfate diffusing from sea water at the interface between these 605 two zones, known as the Sulfate-Methane Transition Zone (SMTZ). The SMTZ typically lies a 606 few meters to a few tens of meters below seabed in normal conditions. The reaction is 607 mediated by a Bacteria / Archaea consortium that produces hydrogen sulfide and HCO₃ 608 [Boetius et al., 2000; Orphan et al., 2001; Reeburgh, 1976; Valentine & Reeburgh, 2000]. 609 When dissolved methane is actively supplied from deeper zones, its flux can result in the 610 consumption of the entire sulfate available in the shallow section, so that the SMTZ may be 611 pushed up to the seabed by dissolved methane in excess. In that case, dissolved methane 612 can feed benthic life and escape into the water column [Gay et al., 2006a], as observed in 613 the Spider Structures.

As shown by Figures 4.C and 8.B, the regional background (Morphotype A) shows neither
seabed reflectivity nor amplitude anomalies in the subbottom, indicating that the limited
methane flux observed there is insufficient to promote any significant carbonate
development.

618 The more moderate CH₄ concentrations associated with bacterial mats observed over 619 Morphotype B indicate moderate and possibly episodic fluxes of dissolved methane there. 620 This ongoing venting of gas can only sustain the growth of microbial mats and locally of 621 bivalve communities; conversely, the higher concentrations observed above Morphotype C 622 attest to a higher and likely more permanent flux there, resulting in the development of 623 thriving biological communities [Gay et al., 2006b]. The presence of carbonates over 624 Morphotype C implies that even if the measured methane concentrations are quite low, 625 compared for instance to what has been observed on the Regab pockmark (10 to 100 times 626 higher) in the same basin [Ondréas et al., 2005], methane fluxes must have been high and 627 sustained enough over a long time to allow the formation of the massive carbonates 628 observed on Morphotype C for instance (Fig. 10D, 10E, 10F). On the contrary, the low 629 concentrations of dissolved methane recorded above Morphotype A are clearly insufficient 630 to promote the development of carbonate precipitation at the seabed. Overall, the 631 comparison between CH₄ concentrations and the presence or absence of carbonates on 632 Morphotypes A, B and C is interpreted to indicate that significant carbonate bodies can only develop at the seabed in conditions of high and steady enough methane supply. 633

634

635 Origin of fluids

636 The next issue is the provenance of the seeping methane; it will be addressed using the637 isotope analyses of the carbon and oxygen of the carbonates. First, the carbon isotopic

638 composition of authigenic carbonates serves as an indicator for the origin of carbon

639 incorporated during carbonate precipitation [Anderson & Arthur, 1983; Reeburgh, 1980;

640 Ritger *et al.,* 1987].

The carbon isotope composition (δ^{13} C) of shell fractions collected at sites 2 and 3 on Morphotype C (see Fig.3 for location) are -3.1 ‰ and 2.1 ‰ (Fig.13). These values are very close to the shell group defined by [Campbell, 2006], indicating that the carbon corresponds to dissolved inorganic carbon from seawater [Campbell, 2006; Judd & Hovland, 2007]. The two cement fractions of carbonate samples collected on Morphotype C have a very similar carbon isotopic composition with negative values of δ^{13} C: -35.5 ‰ at site 2 and -34.3 ‰ at site 3 (Fig.13).

648 According to Aharon et al., 1997 and Whiticar, 1999, sources of carbon to the pore fluids include (1) biogenic methane (δ^{13} C <-65 ‰ PDB) or thermogenic methane (δ^{13} C from -30 ‰ 649 to -50 ‰); (2) sedimentary organic carbon (δ^{13} C ~ -25 ‰); and (3) marine biogenic 650 carbonate or seawater CO_3^{2-} with a δ^{13} C value close to 0 ‰. The amount of mixing between 651 these different sources will determine the δ^{13} C value of any authigenic carbonate [Paull *et* 652 *al.*, 1992]. According to [Campbell, 2006], the δ^{13} C value close to -35‰ measured on studied 653 654 samples is located at the junction of three possible carbon sources (1) sedimentary organic diagenesis (-15 ‰ < δ^{13} C<-35 ‰), (2) oil fractions (-20 ‰ < δ^{13} C<-35 ‰) and (3) thermogenic 655 methane (-40 ‰< δ^{13} C<-50 ‰) (Fig.13). Although the measured values of δ^{13} C are not 656 657 conclusive by themselves here: they are compatible with an origin from thermogenic 658 hydrocarbons, but also from a combination of biogenic methane and normal marine 659 carbonates.

660 The stable oxygen isotopic composition of authigenic carbonates provides further661 information about environmental conditions such as the fluid source and temperature

during precipitation [Han et al., 2004; Kim et al. 2007]. Carbonate precipitation is 662 accompanied by a temperature-dependent oxygen isotope fractionation relative to the 663 water from which the carbonates precipitate. The δ^{18} O carbonate isotope analyses of the 664 four samples show homogeneous values close to 4 ‰ V-SMOW (from 3.6 to 4.3 ‰, Fig.13, 665 Table 1), with no significant variations at sites 2 and 3 indicating uniform conditions during 666 carbonate growth at the seafloor. According to Rohling, 2013, the values of δ^{18} O in surface 667 668 water range worldwide between -7 ‰ in polar waters and +2 ‰ in tropical waters, and the 669 values along the west coast of Africa lie between + 0.5 and +1 ‰. In that respect, the observed values around +4 ‰ are anomalous. Such anomalously positive δ^{18} O value of 4 ‰ 670 V-SMOW have commonly been observed in seep carbonates resulting from gas hydrate 671 672 dissociation [Bohrmann et al., 1998; Feng et al., 2010; Greinert et al., 2001; Haas et al., 2010]. This is due to the fact that the water in the gas hydrate cages is enriched in 18 O by 673 674 2 ‰ to 3 ‰ relative to the primary pore-waters [Davidson et al., 1983; Ussler & Paull, 1995]. The positive anomaly of δ^{18} O measured at both sites can thus be related to gas hydrate 675 676 dissolution in underlying sediments.

Isotopic analyses are therefore not conclusive as regards the origin of the seeping methane; 677 678 in other terms, both thermogenic hydrocarbons coming from the deep and biogenic gas 679 generated in the shallow section could fuel the Spider Structures. The main indication for the 680 distribution of dissolved methane in the area is provided by the two patches of BSR underneath the two Spider Structures (Fig.6). They are located right above two underlying 681 682 vertical zones of reduced amplitude connecting at depth with Miocene turbidite channels 683 (Fig.6). Hydrates are stable only in dissolved methane-saturated water [Lapham et al., 2010], 684 i.e. in the presence of a continuous flux of gas (dissolved at saturation level or in gaseous 685 state). Local generation of biogenic gas in the shallow section is not supported by any 686 seismic observation, and it seems difficult to envision the presence of localized patches of

organic matter in the hemipelagic context of the Pliocene of the area [Uenzelmann-Neben,

1998]. The most likely source for the seeping methane is thus the underlying Miocene

reservoir. The next section will discuss the possible migration pathway for the methane from

690 the reservoir up to the Spider Structures.

691 Fluid pathways

The presence of gas hydrates (whose formation requires active methane supply) just above the local culmination of the underlying hydrocarbon reservoir, and there only, strongly suggests that methane is actively migrating vertically up from the Miocene reservoirs to the BSR (but not necessarily as free gas). There are two main pathways for fluids through a sedimentary column, along fault planes and within fluid pipes [Gay et al., 2007].

697 In the study area, major normal faults are associated with slight linear depressions on the 698 seafloor (Fig.3&6). However, they are not directly related to gas venting sites, except where 699 they cross Miocene turbidite channels at depth. Here, deep-rooted faults individualized 700 several half-grabens (Fig.6). The two patches of BSR and the two related seafloor seep sites 701 are located over the crest of a horst block forming local culminations of the Miocene 702 reservoirs. This suggests that the structural tops of the Miocene reservoirs act as leakage 703 points for upward hydrocarbon migration. Some high-amplitude anomalies have been 704 identified at variable levels at depth along major fault planes with variable polarities and 705 may represent seep carbonates indicating past occurrence of gas seepage along some of the 706 faults (positive amplitudes) or minor gas accumulations trapped in local reservoirs (negative 707 patches).

The Pliocene to Present interval is highly affected by polygonal faulting [Gay *et al.,* 2004].
Polygonal faults may act as migration conduits for driving up fluids entrapped within
underlying sandy reservoirs [Gay *et al.,* 2004; Lonergan *et al.,* 2000], it has recently been

argued that they could also seal early after burial in the same Lower Congo Basin, on the
basis of a detailed analysis of the geometric relationships between high impedance seismic
anomalies and polygonal fault pairs [Ho et *al.*, 2016]. There is no clear evidence on our
dataset that these faults played any role in the formation of the Spider Structures in the
area.

716 Both patches of BSR are partly underlain by columns of low-amplitude, commonly fuzzy 717 reflections down to the top of the Miocene reservoirs; locally, these columns slightly widen 718 downward (Fig.6.B). They could correspond either to an acoustic masking effect by the 719 shallow free gas trapped under the BSR, or real evidence for the presence of free gas 720 bubbles attenuating the signal. The only difference between these two hypotheses is the 721 thickness of free-gas-bearing sediment: a few meters or tens of meters in the former, or the 722 full column from reservoir to BSR in the latter. The seismic cube was processed for 723 amplitude vs. offset studies (AVO), and both short and long offset cubes are available. 724 Undershooting by far seismic offsets should narrow down the masking window at depth, 725 while a continuous gas column down to the reservoir should have the same geometry on 726 short and long offset data. A comparison of short and long offset cubes was undertaken, but 727 did not prove conclusive due to the differences in frequency content between the two 728 cubes.

Whatever the case, the patches of BSR match the local culminations of the underlying reservoirs. If the gas migrated along the normal faults that affect the series, i.e. along oblique surfaces with a dip of ca. 45°, the BSR should be offset in the upslope direction of the faults. This is not the case, so that fault control on gas migration is negligible. As mentioned in the previous section, independent in situ generation of biogenic gas in the section overlying the reservoirs would imply that patches of source rock were deposited right above the culmination of the underlying reservoirs, which does not seem to make

sense. We therefore conclude that gas migrated vertically upward through the seal, withoutbeing affected by faults.

738

739 Methane seepage evolution over geological time

740 Buried carbonates and seabed fluid fluxes in Morphotype B

741 The envelope display of a 2D-AUV profile across Morphotype B shows closely spaced patches 742 of high amplitude buried within the first 60 ms TWT below the main seafloor depression of 743 Morphotype B (Fig.8.A&B). In fluid venting zones, on siliciclastic mud-dominated slopes, 744 positive high amplitude patches on seismic data are generally interpreted as the response of 745 buried carbonate concretions [Bayon et al., 2009; Ho et al., 2012; Römer et al., 2014; Savini 746 et al., 2009]. These patches thus seem to correspond to buried seep carbonates that mainly 747 concentrate along four laterally discontinuous levels under the depression of Morphotype B 748 (Fig.8). The distribution of amplitude anomalies into four levels suggests that fluid venting 749 activity has been recently higher than at the present day [Stakes et al., 1999], with periods of 750 massive dissolved gas release alternating with periods of low to very low seafloor fluid 751 venting, possibly representing self-sealing of the seeps [Gay et al., 2006b; Hovland, 2002]. 752 The four levels of amplitude patches are not present on each high-resolution 2D seismic 753 profile, and each level has a different lateral extension. The two deepest levels concentrate 754 in the western part of the main depression (Fig.8), meaning that fluid venting was initially 755 more active in this area. The two shallowest levels are more heterogeneous with high to 756 very high amplitude patches (Fig.8). This could indicate zones were gas venting activity was 757 locally higher. This has also been observed in the elongated depressions of Morphotype C, where sites of massive dissolved gas release (Fig.12) were correlated with high amplitude 758 759 seafloor anomalies on seismic data (Fig.9). The shallowest level, 10 ms TWT thick, is made of

760 densely distributed high amplitude patches. This interval is buried at about 10 ms TWT 761 below seafloor and it was identified on all high resolution 2D seismic profiles crossing 762 Morphotype B. This suggests that the episode of massive dissolved gas release responsible 763 for the formation of this uppermost concretion-bearing interval affected the entire 764 depression of Morphotype B. Morphotype B consists of two ellipsoidal flat-bottomed and 1-765 3 meters deep depressions with smooth edges (Fig.4.A&B). They are characterized by 766 medium coherency values, indicating a rough bottom or subbottom due to the 767 heterogeneous distribution of the sub-seafloor anomalies. They are also characterized by a 768 very low backscatter reflectivity (Fig.4.C), similar to the regional slope reflectivity. The 769 vertical resolution of the latter tool being a few cm, this means that there is no buried hard 770 structures are present in the first few cm below seafloor in Morphotype B. The bottom of 771 Morphotype B only revealed the presence of wide white patches of bacterial mat settled on 772 black reduced sediments, but neither associated with benthic life, nor with carbonate slabs (Fig.10.A-B). The low concentrations of dissolved methane with relatively low concentrations 773 774 of dissolved Mn and Fe suggest a rather diffuse and low fluid venting activity. The patch of 775 Morphotype B can thus be considered as a dying site, which is being draped by hemipelagic 776 sediments and currently undergoing a low gas venting activity with low and probably discontinuous release of dissolved methane in the water column. 777

778

Seabed carbonates and fluid fluxes in Morphotype C

Where 2D-AUV profiles cross elongated depressions of Morphotype C, the seismic profiles show high amplitude patches located in the immediate sub-seafloor section (Fig.9). The size of these high-amplitude patches mostly depends on the width of the associated seafloor elongated depressions. The high amplitude patches visible on seismic data, are usually associated with an underlying acoustic blanking effect (Fig.9), which is quite commonplace on high-resolution shallow seismic profiles in areas where gas is present [Judd & Hovland,

785 2007]. At the seafloor, Morphotype C is characterized by low values of coherency (Fig.4.-D), 786 and high values of backscatter reflectivity, more particularly in the broadest depressions 787 (Fig.4.C). This means that there is a significant contrast in lithology between the regional 788 slope made of hemipelagic sediments and the bottom of elongated depressions. The in-situ 789 seafloor observations obtained during ROV dives confirmed that the depressions of 790 Morphotype C correspond to carbonates as massive slabs, nodules and tubes with a central 791 conduit (Fig.10.C to 10.F, Fig.11); the distribution of carbonates matches the extent of the 792 high-coherency and high-reflectivity depressions. The authigenic carbonates of 793 Morphotype C are associated with the extensive occurrence of microbial mats on blackish 794 reduced, flat sediments outcropping between carbonate concretions (Fig.10.F), indicating 795 widespread intense hydrocarbon seepage and active microbial dissolved methane 796 conversion via anaerobic oxidation of methane [Römer et al., 2014]. Carbonate slabs can 797 form massive and large slabs many of which are tilted; this leads to the exhumation of a part 798 of the slab while the other part is buried in the surrounding hemipelagic sediments (Fig.10.D-799 E). Most of these slabs, besides being tilted, are fractured and form several fragments, some 800 of which collapsed onto the mud-covered floor of the adjacent furrow (Fig.10.D). The 801 nodular and tubular carbonates with central conduits are partly buried although they 802 generally form within the sediments suggesting a later erosion of covering hemipelagic 803 sediments (Fig.10.C). The presence of authigenic carbonate slabs associated with an 804 abundant benthic life as tubeworms and bivalves (Fig.10.E) is an indicator for sustained seep 805 activity [Gay et al., 2006b; Macelloni et al., 2013; Olu et al., 2009].

806

Temporal evolution

The vertical evolution of seismic reflectivity observed in subseafloor from level 1 to level 4 and at the seabed thus indicates that the high flux of dissolved methane seepage was

809 initially concentrated in the western part of Morphotype B and progressively migrated

eastwards. It is presently concentrated in Morphotype C, which is located E-SE of
Morphotype B. This means that the lateral migration of the fluid seepage, since the
emplacement of the deepest anomaly identified at 60 ms TWT below seafloor, has been
following the same direction over time corresponding to an E-SE (i.e. upslope) migration of
the fluid seepage.

815 We tried to assess the temporal variation of the fluid venting activity within the 816 spider structure by estimating the sedimentation rate and then the ages of the buried levels 817 of high amplitude under Morphotype B. The Pliocene interval of the study area is 818 approximately 1 s twt thick. We used this assessment to estimate the sedimentation rate 819 during the Pliocene interval, assuming an average velocity of 1800 m/s for the interval. The 820 sedimentation rate with these parameters is estimated at around 20 cm/ky. This value is 821 consistent with the sedimentation rates obtained in the shallower 80 m on ODP (Ocean 822 Drilling Program) well 1076, which is 30 cm/ky. The deepest seismically visible level under 823 Morphotype B (level 1) is located at around 60 ms twt below seafloor, corresponding to 824 around 45 m with a velocity of 1500 m/s in the shallow subsurface [Sultan et al. 2007]. Using 825 the locally estimated sedimentation rate, Level 1 is dated at ca. 0.2 Ma, which would 826 indicate that spider structure 1 has been active since the Ionian stage of the Pleistocene.

The shallowest anomaly (level 4) ca. 10 m below seabed could be dated around 50 ka with this estimate. Keeping in mind that the upper 10 m are significantly less compacted than deeper level, this value is likely to be a maximum.

830

831 Origin of the depression

Careful picking of the high-resolution 2D-AUV seismic profile crossing Morphotype B hasshown that background horizons could be followed into the domain covered by Morphotype
834 B (the seafloor depression) and that they show some downward bending below the edge of 835 that domain. Figure 8.C indicates that horizons are affected down to below Level 1, 836 suggesting local removal of material over the area of Morphotype B, below the deepest seep 837 carbonate interval (Level 1). Along with the presence of hydrates interpreted from the BSR 838 underneath, this sagging is interpreted to reflect hydrate dissociation and removal like in 839 hydrate pockmarks observed in Nigeria [George & Cauquil, 2007] and documented by 840 [Sultan et al., 2010]. The dimming of the reflections below Morphotype B makes it difficult 841 to see whether sagging occurred in one episode or progressively over time.

842 Genetic model of the Spider Structure

1.

843

Present-day situation

At present, both Spider Structures exhibit a similar style of venting, with lower activity in Morphotype B and higher activity in Morphotype C. The former is just sufficient to feed microbial mats at the seafloor and give a CH4 concentration in surface sediments that exceeds the local background by a factor 3 or 4. In Morphotype C, CH4 concentration is about 3 times higher than in Morphotype B of the same Spider.

The morphology of the two morphotypes are very contrasted, B being smooth and very uniform whereas Morphotype C shows long furrows separated by plateaus of smooth seabed. Carbonates are widespread at the floor of the furrows and in their banks.

As regards hydrates, Morphotype B is underlain by a continuous patch of BSR, while the BSR
is much more subdued and discontinuous below Morphotype C. No BSR can be seen in areas
of background Morphotype A.

855 Morphotype A corresponds to very limited CH4 supply if any, Morphotype B to areas of 856 uniform low flux and Morphotype C to a clustering of linear domains of flux high enough to 857 sustain abundant chemosynthetic life.

Let us now examine the recent evolution of the flux, integrating the shallow subsurface information below Morphotype B.

Evolution since the most recent carbonate (from level 4 to present)
 Combining now subsurface observations with seafloor observations and analyses, it is
 possible to propose an evolutionary model depicting the two morphotypes as successive
 stages of evolution of the leakage system, as follows:

864 Active gas venting activity at the giant pockmark (MB) a) In an early phase, methane migrating from the Miocene reached the seabed with fluxes high 865 866 enough to promote the development of seep carbonates below what is currently 867 Morphotype B (level 4 on Fig.8). Methane hydrates may have started to form during this 868 phase or not; in any case, enough gas was supplied / the BSR was discontinuous enough to 869 let abundant methane pass upwards through it and reach the seabed. Figure 14.A depicts 870 the situation at that time, showing the situation where the hydrate BSR was beginning to 871 form in the area. No venting activity could be recorded below the "legs" of the spiders at 872 that time

873

874

b) Upslope shifting of the gas venting activity, from the giant pockmark (MB) to elongated pockmarks (MC)

At a certain point in time, the development of porosity-clogging hydrates was such that upwards migration of methane significantly decreased at Morphotype B, as shown on Fig. 14.B. Methane went on diffusing from the hydrates above the BSR upwards to the seafloor through diffusion, with possibly some additional advective flux along fractures or other preferential pathways. This residual flux is able to sustain the growth of microbial mats, with the local development of small communities of pelecypods, but not to promote the development of widespread full communities as observed on Morphotype C. From this point

882 on, the former seep carbonates were progressively buried by hemipelagic drape that smoothed the seabed over Morphotype B. 883

884 The dissolution of hydrates in the lower part of the hydrate stability zone (above the 885 impervious BSR) results in progressive subsidence of the overlying series, forming the 886 seafloor depression. The body of the spider can thus be viewed as a progressively collapsing 887 hydrate pockmark, as described by [Wei et al., 2015] for an active example or [Imbert & Ho, 888 2012] for a cluster of fossil equivalents

889 *c*) Setting of the current gas venting activity in elongated 890 pockmarks (MC)

891 When there were enough hydrates to significantly decrease methane flux at Morphotype B, 892 incoming methane was redirected below the BSR overall acting as seal and shifted upslope 893 to the area of Morphotype C (Fig. 14.C). Methane venting is currently ongoing there, as 894 evidenced by the thriving biological communities present in and around the furrows, and it 895 has been active long enough for thick carbonate crusts to develop. The furrows are 896 interpreted as the linear equivalent of pockmarks, where leakage is responsible for removal 897 of fine-grained material and excavation of the furrows. The reason of this focusing of 898 dissolved gas along linear features is not clear yet: some furrows appear to follow very 899 shallow faults (less than 100 ms twt deep) while others develop without seismic evidence for a fault, at least with the resolution of the seismic data. 900

- 901
- 3. Speculative evolution of the fluid venting activity below the giant 902 pockmark (MB), over four carbonate levels

903 How did the Spider Structures form in the first place? This section will propose a few elements that could guide further reflection about the issue, based on the previous 904

905 discussed points, the presence of 4 stacked interpreted carbonate levels below Morphotype906 B and the estimated timing.

907 The estimate we could make for the full duration of the 4 successive stacked levels of 908 interpreted carbonates underneath Morphotype B is ca. 200 ky. This is clearly to take as an 909 order of magnitude, regarding the uncertainties on the precise rate of sedimentation in the 910 area and its possible fluctuations through time. Using the same estimate, the emplacement 911 of the upper level 4 could be dated around 50 ka. One possibility would be to have the 4 912 carbonate levels associated with the last 4 major low sea-level stands of the Quaternary ca. 913 350 ka (MIS 9), ca. 250 ka, ca. 150 ka and ca. 20 ka. [Lobo & Ridente]. We speculate that 914 these may correspond to times when the wedge of hydrates was displaced seaward of the 915 Spider Structures, so that the full methane supply could reach the seabed directly.

916 Conclusion

917 Our multidisciplinary study of a site of dissolved methane leakage above a hydrocarbon-

918 bearing reservoir has evidenced a specific type of gas escape feature, undocumented so far.

919 This type of seabed anomaly, here called the "Spider Structure" has the following

920 characteristics:

A Spider Structure is comprised of a sub-circular, depression ("body" of the spider)
from which a set of multi-m-deep furrows ("legs") protrude, dominantly upslope
In our study area, both the "body" and "legs" leak dissolved methane into the water
column, but the "body" shows limited activity while the "legs" are very active.
The two "spiders" we observed lie above the structural crest of an oil and gas
reservoir, some 900 m below; patches of hydrate BSR are visible just below the body
of each spider, about 100 m below seabed.

- Visual observation and sampling show carbonates at or just below the seabed in the
 "legs" of the spiders. Isotopic analysis indicates that these carbonates result from
 anaerobic oxidation of thermogenic methane.
- The "body" in underlain by at least 4 seismic horizons rich in patches of high impedance material (interpreted as seep carbonates) in the uppermost 100 m of the
 sedimentary column.
- These seep carbonate levels are 10 to 20 m apart vertically, the shallowest being ca.
 10 m below present-day seabed. The vertical stack is interpreted to reflect temporal
 variations in the emitted flux of dissolved methane.
- The activity of the seeps has been shifting upslope over time, with early stages
 essentially developed in the most downslope part of the "body", subsequent ones
 filling the whole body, while at present the body is moribund and most of the
 dissolved gas currently leaks from the "legs".
- The shift from "body" to "legs" is interpreted to reflect self-sealing of the hydrate
 BSR over time, as more dissolved gas is supplied since the base hydrate stability zone
 (GHSZ) reached its present position at the end of the Holocene transgression. The
 body still records episodic leakage of low fluxes, reflecting progressive dissolution of
 the starving upper part of the GHSZ.

This model makes the "Spider Structure" one highly dynamic end-member of the spectrum
of hydrate-related leakage features, like hydrate pingoes, mounds and pockmarks. The body
is comparable in many respects to hydrate pockmarks described in literature, with a
dissociating body at depth leading to some collapse upon hydrate dissolution. The legs could
be seen as a precursor stage of the leakage, before hydrate growth makes a continuous layer
and clogs the leakage points. A "spider structure" would then be a snapshot of the shift from

- 952 a dying early activity distributed over a subcircular patch and a later, more juvenile activity
- 953 restricted to a network of furrows located upslope of the subcircular patch.
- 954 The present study has deciphered the recent evolution of the two "Spider Structures" of the
- 955 area. The study of deeper anomalies on the available 3D seismic surveys should lead to a
- 956 better understanding of the long-term evolution of the leakage system.

957 Acknowledgments:

- 958 The authors would like to acknowledge Total for the access to seismic dataset and for
- 959 financing the PhD work of Viviane Casenave. The authors would like to thank Ifremer for the
- 960 access to the ZAIANGO dataset and Eric Cauquil (TOTAL) for his stimulating insight and
- 961 encouragements to undertake this study. We also thank Sidonie Révillon for her contribution
- 962 in carbonate isotopic analysis. We would like to thank the reviewers D. Praeg and N. Sultan
- 963 for their helpful suggestions and constructive comments.
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971 **References**

972 AH/	ARON P.,	SCHWARCZ H.P	. & ROBERTS H.H.	(1997).	- Radiometric da	ting of	submarine
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- 973 hydrocarbon seeps in the Gulf of Mexico. *Geological Society of America Bulletin*, **109**, 5,
 974 568-579.
- 975 ANDERSON T.F. & ARTHUR M.A. (1983). Stable isotopes of oxygen and carbon and their
- 976 applications to sedimentologic and paleoenvironmental problems. In: ARTHUR M.A.,
- 977 ANDERSON T.F., KAPLAN I.F., VEIZER J. & LAND L.S., Eds., Stable Isotopes in Sedimentary
- 978 Geology. SEPM Short Course, **10**.
- 979 ANDRESEN K.J., HUUSE M., SCHØDT N.H., CLAUSEN L. F. & SEIDLER L. (2011). Hydrocarbon
- 980 plumbing systems of salt minibasins offshore Angola revealed by three-dimensional seismic
- 981 analysis. AAPG Bulletin, **95**, 1039-1065
- 982 BABONNEAU N., SAVOYE B., CREMER M. & KLEIN B. (2002). Morphology and architecture
- 983 of the present canyon and channel system of the Zaire deep-sea fan. Marine and Petroleum
- 984 *Geology*, **19**, 445- 467.
- 985 BAHORICH M. & FARMER, S. (1995). 3-D seismic discontinuity for faults and stratigraphic
- 986 features: The coherence cube. *The Leading Edge*, **14**, 10, 1053-1058
- 987 BARTEK L.R., VAIL P.R., ANDERSON J.B., EMMET P.A. & WU, S. (1991). Effect of Cenozoic ice
- 988 sheet fluctuations in Antartica on the stratigraphic signature of the Neogene. Journal of
- 989 *Geophysical Research*, **96**, B4, 6753–6778.
- BAYON G., LONCKE L., DUPRÉ S., CAPRAIS J. C., DUCASSOU E., DUPERRON S., ... & WOODSIDE
- 991 J. (2009). Multi-disciplinary investigation of fluid seepage on an unstable margin: the case
- 992 of the Central Nile deep sea fan. *Marine Geology*, **261**, 1, 92-104.

- 993 BEGLINGER S.E., DOUST H. & CLOETINGH S. (2012). Relating petroleum system and play
- 994 development to basin evolution: West African South Atlantic basins. *Marine and Petroleum*995 *Geology*, **30**, 1–25.
- 996 BERNDT C., BÜNZ S., CLAYTON T., MIENERT J. & SAUNDERS, M. (2004). Seismic character of
- 997 bottom simulating reflectors: Examples from the mid-Norwegian margin. Marine and
- 998 *Petroleum Geology,* **21**, 6, 723-733.
- 999 BOETIUS A., RAVENSCHLAG K., SCHUBERT C. J., RICKERT D., WIDDEL F., GIESEKE A., ... &
- 1000 PFANNKUCHE O. (2000). A marine microbial consortium apparently mediating anaerobic
- 1001 oxidation of methane. *Nature*, **407**, 623-626.
- 1002 BOHRMANN G., GREINERT J., SUESS E. & TORRES M. (1998). Authigenic carbonates from
- the Cascadia subduction zone and their relation to gas hydrate stability. *Geology*, **26**, 7,
- 1004 647-650.
- 1005 BOURIAK S., VANNESTE M. & SAOUTKINE A. (2000). Inferred gas hydrates and clay diapirs
- 1006 near the Storegga Slide on the southern edge of the Vøring Plateau, offshore Norway. -
- 1007 *Marine Geology*, **163**, 125–148.
- 1008 BRICE S.E., COCHRAN M.D., PARDO G. & EDWARDS A.D. (1982). Tectonics and
- 1009 sedimentation of the South Atlantic rift sequences: Cabinda, Angola. American Association
- 1010 of Petroleum Geologists Memoir, **34**, 5-18.
- 1011 BROUCKE O., TEMPLE F., ROUBY D., ROBIN C., CALASSOU S., NALPAS T. & GUILLOCHEAU F.
- 1012 (2004). The role of deformation processes on the geometry of mud-dominated turbiditic
- 1013 systems, Oligocene and Lower–Middle Miocene of the Lower Congo Basin (West African
- 1014 Margin). Marine and Petroleum Geology, 21, 327-348.

- 1015 BROWN A.R. (2011). Color, Character and Zero-Phaseness. In: BROWN A.R. Ed,
- 1016 Interpretation of three-dimensional seismic data. AAPG Memoir 42 and SEG Investigations
- 1017 *in Geophysics,* No. 9, 31-61.
- 1018 BÜNZ S. & MIENERT J. (2004). Acoustic imaging of gas hydrate and free gas at the Storegga
- 1019 Slide. Journal of Geophysical Research , 109, B04102, 1-15.
- 1020 BURWOOD R. (1999). Angola: source rock control for Lower Congo Coastal and Kwanza
- 1021 Basin petroleum systems. In: CAMERON N.R., BATE R.H. & CLURE V.S., Eds., The Oil and Gas
- 1022 Habitats of the South Atlantic. *Geological Society of London*, **153**, 181-184.
- 1023 CAMPBELL K. A. (2006). Hydrocarbon seep and hydrothermal vent paleoenvironments and
- 1024 paleontology: Past developments and future research directions. Palaeogeography,
- 1025 *Palaeoclimatology, Palaeoecology*, **232**, 362-407.
- 1026 CARTWRIGHT J., HUUSE M. & APLIN, A. (2007). Seal bypass systems. *AAPG bulletin*, **91**, 8,
 1027 1141-1166.
- 1028 CARTWRIGHT J. (2011). Diagenetically induced shear failure of fine-grained sediments and
- 1029 the development of polygonal fault systems. Marine and Petroleum Geology, 28, 1593-

1030 1610.

- 1031 CHARLOU J.-L. & DONVAL J.-P. (1993). Hydrothermal methane venting between 12°N and
- 1032 26°N along the Mid-Atlantic Ridge. *Journal of Geophysical Research*, **98**, 9625-9642.
- 1033 CHARLOU J. L., FOUQUET Y., BOUGAULT H., DONVAL J. P., ETOUBLEAU J., JEAN-BAPTISTE P.,
- 1034 ... & RONA P.A. (1998). Intense CH 4 plumes generated by serpentinization of ultramafic
- 1035 rocks at the intersection of the 15 20' N fracture zone and the Mid-Atlantic Ridge. -
- 1036 *Geochimica et Cosmochimica Acta*, **62**, 13, 2323-2333.

- 1037 CHARLOU J. L., DONVAL J. P., ZITTER T., ROY N., JEAN-BAPTISTE P., FOUCHER J. P., ... & PARTY
 1038 M. S. (2003). Evidence of methane venting and geochemistry of brines on mud volcanoes of
 1039 the eastern Mediterranean Sea. *Deep Sea Research Part I: Oceanographic Research Papers*,
 1040 **50**, 8, 941-958.
- 1041 CHEONG C., NONOSE N., MIURA T. & HIOKI A. (2014). Improved accuracy of determination
- 1042 of dissolved silicate in seawater using absorption spectrometry. Accreditation and Quality
- 1043 *Assurance*, **19**, 1, 31-40.
- 1044 COLE G.A., REQUEJO A.G., ORMEROD D., YU Z. & CLIFFORD A. (2000). Petroleum
- 1045 geochemical assessment of the Lower Congo Basin. In: MELLO M.R. & KATZ B.J., Eds.,
- 1046 Petroleum systems of South Atlantic margins. American Association of Petroleum
- 1047 *Geologists Memoir*, **73**, 325-339.
- 1048 CUNNINGHAM R. & LINDHOLM R.M. (2000). Seismic evidence for widespread gas hydrate
- 1049 formation, offshore West Africa. In: MELLO M.R. & KATZ B.J., Eds., Petroleum systems of
- 1050 South Atlantic margins. *American Association of Petroleum Geologists Memoir*, **73**, 93-105.
- 1051 DAFNER E.N., OBZHIROV A.I. & VERESHZHAGINA O.F. (1998). Distribution of methane in
- waters of the Okhotsk and western Bering Seas, and the area of Kuril Islands. *Hydrobiologia* **362**, 93-101.
- 1054 DAVIDSON D. W., LEAIST D. G. & HESSE R. (1983). Oxygen-18 enrichment in the water of a
- 1055 clathrate hydrate. *Geochimica et Cosmochimica Acta*, **47**, 12, 2293-2295.
- 1056 DILLON W.P., GROW J.A. & PAULL C.K. (1980). Unconventional gas hydrate seals may trap
- 1057 gas off southeast U.S. Oil and Gas Journal, 78, 1, 124-130.
- 1058 DROZ L., RIGAUT F., COCHONAT P. & TOFANI R. (1996). Morphology and recent evolution of
- 1059 the Zaire turbidite system (Gulf of Guinea). Geological Society of America Bulletin, 108,
- 1060 253-269.

- 1061 DUAN Z.H. & MAO S.D. (2006); A thermodynamic model for calculating methane solubility,
- 1062 density and gas phase composition of methane-bearing aqueous fluids from 273 to 523 K
- 1063 and from 1 to 2000 bar. *Geochim. Cosmochim. Acta.*, **70**, 13, 3369-3386.
- 1064 DUVAL B., CRAMEZ C. & JACKSON M.P.A. (1992). Raft tectonics in the Kwanza Basin,
- 1065 Angola. *Marine and Petroleum Geology*, **9**, 389-404.
- 1066 FENG D., CHEN D., PECKMANN J. & BOHRMANN G. (2010). Authigenic carbonates from
- 1067 methane seeps of the northern Congo fan: microbial formation mechanism. *Marine and*
- 1068 *Petroleum Geology*, **27**, 4, 748-756.
- 1069 FIELD M.E. & KVENVOLDEN K.A. (1985). Gas hydrates on the northern California continental
- 1070 margin. *Geology*, **13**, 517-520.
- 1071 FORT X., BRUN J.-P. & CHAUVEL F. (2004). Contraction induced by block rotation above salt
- 1072 (Angolan margin). *Marine and Petroleum Geology*, **21**, 1281–1294.
- 1073 FOUCHER J.P., WESTBROOK G.K., BOETIUS A., CERAMICOLA S., DUPRE S., MASCLE J.,
- 1074 MIENERT J., PFANNKUCHE O., PIERRE C. & PRAEG D. (2009) Structure and drivers of cold
- 1075 seep ecosystems. *Oceanography*, **22**, 1, 92-109.
- 1076 GAY A., LOPEZ M., COCHONAT P. & SERMONDADAZ G. (2004). Polygonal fault-furrows
- 1077 system related to early stages of compaction upper Miocene to recent sediments of the
- 1078 Lower Congo Basin. *Basin Research*, **16**, 101–116.
- 1079 GAY A., LOPEZ M., COCHONAT P., LEVACHÉ D., SERMONDADAZ G. & SERANNE M. (2006a). -
- 1080 Evidences for early to late fluid migration from an upper Miocene turbiditic channel revealed
- 1081 by 3D seismic coupled to geochemical sampling within seafloor pockmarks, Lower Congo
- 1082 Basin. *Marine and Petroleum Geology*, **23**, 387-399.

- 1083 GAY A., LOPEZ M., COCHONAT P., SÉRANNE M., LEVACHE D. & SERMONDADAZ G. (2006b). -
- 1084 Isolated sea floor pockmarks linked to BSRs, fluid chimneys, polygonal fault sand stacked
- 1085 Oligocene–Miocene turbiditic paleochannels in the lower Congo Basin. *Marine Geology*,
 1086 **226**, 25-40.
- 1087 GAY A., LOPEZ M., BERNDT C. & SÉRANNE M. (2007). Geological controls on focused fluid
- 1088 flow associated with seafloor seeps in the Lower Congo Basin. *Marine Geology*, **244**, 68-92.
- 1089 GEORGE R.A. & CAUQUIL E. (2007). AUV Ultra High-Resolution 3D Seismic Technique for
- 1090 Detailed Subsurface Investigations. In : Offshore Technology Conference. Offshore
- 1091 Technology Conference. ISBN978-1-55563-254-0
- 1092 GREINERT J., BOHRMANN G. & SUESS E. (2001). Gas hydrate-associated carbonates and
- 1093 methane-venting at Hydrate Ridge: classification, distribution and origin of authigenic
- 1094 lithologies. Geophysical Monograph-American Geophysical Union, 124, 99-114.
- 1095 GUILLON S. & KESKES N. (2004, October). Sismage and the 3d visualization at Total. In:
- 1096 American Association of Petroleum Geologists International Conference: October, 24-27.
- 1097 HAAS A., PECKMANN J., ELVERT M., SAHLING H. & BOHRMANN G. (2010). Patterns of
- 1098 carbonate authigenesis at the Kouilou pockmarks on the Congo deep-sea fan. Marine
- 1099 *Geology*, **268**, 1, 129-136.
- 1100 HAN X., SUESS E., SAHLING H. & WALLMANN K. (2004). Fluid venting activity on the Costa
- 1101 Rica margin: new results from authigenic carbonates. International Journal of Earth
- 1102 Sciences, **93**, 4, 596-611.
- HEGGLAND R. (1998). Gas seepage as an indicator of deeper prospective reservoirs. A study
 based on exploration 3D seismic data. *Marine and Petroleum Geology*, **15**, 1-9.

- 1105 HO S., CARTWRIGHT J.A. & IMBERT P. (2012). Vertical evolution of fluid venting structures
- 1106 in relation to gas flux, in the Neogene-Quaternary of the Lower Congo Basin, Offshore
- 1107 Angola. *Marine Geology*, **332**, 40-55.
- 1108 HO, S., CARRUTHERS, D., & IMBERT, P. (2016). Insights into the permeability of polygonal
- 1109 faults from their intersection geometries with Linear Chimneys: a case study from the Lower
- 1110 Congo Basin. *Carnets Geol.*, **16**, 02, 17.
- 1111 HOVLAND M., GARDNER J. V. & JUDD A.G. (2002). The significance of pockmarks to
- 1112 understanding fluid flow processes and geohazards. *Geofluids*, **2**, 127-136.
- 1113 HOVLAND M. & SVENSEN H. (2006). Submarine pingoes: Indicators of shallow gas hydrates
- in a pockmark at Nyegga, Norwegian Sea. *Marine Geology*, **228**, 15–23.
- 1115 HUUSE M., JACKSON C. A.-L., VAN RENSBERGEN P., DAVIES R.J., FLEMINGS P.B. & DIXON R.J.
- 1116 (2010). Subsurface sediment remobilization and fluid flow in sedimentary basins: An
- 1117 overview. Basin Research, **22**, 4, 342-360.
- 1118 INGRASSIA M., MARTORELLI E., BOSMAN A., MACELLONI L., SPOSATO A. & CHIOCCI F.L.
- 1119 (2015). The Zannone Giant Pockmark: First evidence of a giant complex seeping structure in
- shallow-water, central Mediterranean Sea, Italy. Marine Geology, 363, 38-51.
- 1121 IMBERT P. & HO S. (2012). Seismic-scale funnel-shaped collapse features from the
- 1122 Paleocene-Eocene of the Northwest shelf of Australia. *Marine Geology*, **332**, 198-221
- 1123 IVANOV M., BLINOVA V., KOZLOVA E., WESTBROOK G. K., MAZZINI A., MINSHULL T. &
- 1124 NOUZÉ H. (2007). First sampling of gas hydrate from the Vøring Plateau. *Eos, Transactions*
- 1125 *American Geophysical Union*, **88**, 19, 209-212.

- 1126 JANSEN J.H.F., VAN WEERING T.G.E., GIELES R. & VAN IPEREN J. (1984). Middle and late
- 1127 Quaternary oceanography and climatology of the Zaire-Congo fan and the adjacent eastern
- 1128 Angola Basin. *Netherlands Journal of Sea Research*, **17**, 201-241.
- 1129 JUDD A. & HOVLAND M. (2007). Seabed Fluid Flow, the Impact on Geology, Biology and the
- 1130 Marine Environment. Cambridge University Press, Statoil Norway, 290-314.
- 1131 KARNER G.D., DRISCOLL N.W., MCGINNIS J.P., BRUMBAUGH W.D. & CAMERON N.R. (1997). -
- 1132 Tectonic significance of syn-rift sediment packages across the Gabon–Cabinda continental
- 1133 margin. *Marine and Petroleum Geology*, **14**, 7, 973-1000.
- 1134 KIM S. T., O'NEIL J. R., HILLAIRE-MARCEL C. & MUCCI A. (2007). Oxygen isotope
- 1135 fractionation between synthetic aragonite and water: influence of temperature and Mg 2+
- 1136 concentration. *Geochimica et Cosmochimica Acta*, **71**, 19, 4704-4715.
- 1137 LAMMERS S., SUESS E. & HOVLAND M. (1995). A large methane plume east of Bear Island
- 1138 (Barents Sea): implications for the marine methane cycle. *Geologische Rundschau*, **84**, 1,
- 1139 59-66.
- 1140 LAMONTAGNE R.A., SWINNERTON J.W., LINNENBOM V.J. & SMITH W.D. (1973). Methane
- 1141 concentration in various marine environments. J. Geophys. Res. 78, 5317–5324.
- 1142 LAPHAM L.L., CHANTON J.P., CHAPMAN R. & MARTENS C.S. (2010). Methane under-
- saturated fluids in deep-sea sediments: Implications for gas hydrate stability and rates of
- dissolution. *Earth and Planetary Science Letters*, **298**, 3, 275-285.
- 1145 LIRO L.M. & COEN R. (1995). Salt deformation history and postsalt structural trends,
- 1146 offshore southern Gabon, West Africa. In: JACKSON M.P.A., ROBERTS D.G. & SNELSON S.,
- 1147 Eds., Salt tectonics: a global perspective. American Association of Petroleum Geologists
- 1148 *Memoir*, **65**, 323-331.

- 1149 LOBO F.J. & RIDENTE D. (2013). Milankovitch cyclicity in modern continental margins:
- 1150 stratigraphic cycles in terrigenous shelf settings. *Boletín Geológico y. Minero*, **124**, 2, 169-

1151 185.

- 1152 LONERGAN L., LEE N., JOHNSON H.D., CARTWRIGHT J.A. & JOLLY R.J. (2000). Remobilization
- 1153 and Injection in Deepwater Depositional Systems: Implications for Reservoir Architecture
- and Prediction. In: Deep-Water Reservoirs of the World: Gulf Coast Section SEPM
- 1155 Foundation. 20th Annual Conference, Houston, 515-532.
- 1156 LØSETH H., GADING M. & WENSAAS L. (2009). Hydrocarbon leakage interpreted on seismic
- 1157 data. *Marine and Petroleum Geology*, **26**, 7, 1304-1319.
- 1158 LØSETH H., WENSAAS L., ARNTSEN B., HANKEN N.-M., BASIRE C. & GRAUE K. (2011). 1000
- 1159 m long gas blow-out pipes. *Marine and Petroleum Geology*, **28**, 5, 1047-1060.
- 1160 LOVLEY D.R. (1991). Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiological reviews*,
- 1161 **55**, 2, 259.
- 1162 LUNDIN E.R. (1992). Thin-skinned extensional tectonics on a salt detachment, northern
- 1163 Kwanza Basin, Angola. *Marine and Petroleum Geology*, **9**, 405–411.
- 1164 MACELLONI L., BRUNNER C.A., CARUSO S., LUTKEN C.B., D'EMIDIO M. & LAPHAM L.L. (2013).
- 1165 Spatial distribution of seafloor bio-geological and geochemical processes as proxies of fluid
- 1166 flux regime and evolution of a carbonate/hydrates mound, northern Gulf of Mexico. Deep
- 1167 Sea Research Part I: Oceanographic Research Papers, **74**, 25-38.
- 1168 MARCON Y., ONDRÉAS H., SAHLING H., BOHRMANN G. & OLU K. (2014). Fluid flow regimes
- and growth of a giant pockmark. Geology, 42, 1, 63-66
- 1170 MARTON L.G., TARI G.C. & LEHMANN C.T. (2000). Evolution of the Angolan passive margin,
- 1171 West Africa, with emphasis on post-salt structural style. *Geophysical Monograph-American*
- 1172 *Geophysical Union*, **115**, 129-150.

- 1173 MATSUMOTO R., OKUDA Y., HIRUTA A., TOMARU H., TAKEUCHI E., SANNO R., SUZUKI M.,
- 1174 TSUCHINAGA K., ISHIDA Y., ISHIZAKI O., TAKEUCHI R., KOMATSUBARA J., FREIRE A.F.,
- 1175 MACHIYAMA H., AOYAMA C., JOSHIMA M., HIROMATSU M., SNYNDER G., NUMANAMI H.,
- 1176 SATOH M., MATOBA Y., NAKAGAWA H., KAKUWA Y., OGIHARA S., YANAGAWA K.,
- 1177 SUNAMURA M., GOTO T., LU H. & KOBAYASHI T. (2009). Formation and collapse of gas
- 1178 hydrate deposits in high methane flux area of the Joetsu Basin, eastern margin of Japan. -
- 1179 *Journal of Geography*, **118**, 1, 43-71.
- 1180 MASLIN M., OWEN M., BETTS R., DAY S., DUNKLEY JONES T. & RIDGWELL A. (2010). Gas
- 1181 hydrates: Past and future geohazard?- Philosophical Transactions of the Royal Society of
- 1182 London A: Mathematical, Physical and Engineering Sciences, **368**, 1919, 2369–2393.
- 1183
- 1184 MILKOV A.V. & SASSEN R. (2002) Economic geology of offshore gas hydrate accumulations
- and provinces *Marine and Petroleum Geology*, **19**, 1–11.
- 1186 MILKOV A.V., VOGT P.R., CRANE K., LEIN A.Y., SASSEN R. & CHERKASHEV G.A. (2004). -
- 1187 Geological, geochemical, and microbial processes at the hydrate-bearing Hakon Mosby mud
- 1188 volcano: a review. *Chemical Geology*, **205**, 347-366.
- 1189 MILLER K.G., KOMINZ M.A., BROWNING J.V., WRIGHT J.D., MOUNTAIN G.S., KATZ M.E.,
- 1190 SUGARMAN P.J., CRAMER B.S., CHRISTIE-BLICK N. & PEKAR S.F. (2005). The Phanerozoic
- 1191 record of global sea-level change. *Science*, **310**, 1293–1298.
- 1192 MITCHUM JR R.M., VAIL P.R. & THOMPSON III S. (1977). Seismic stratigraphy and global
- 1193 changes of sea level: Part 2. The depositional sequence as a basic unit for stratigraphic
- analysis: Section 2. Application of seismic reflection configuration to stratigraphic
- 1195 interpretation.-, 53-62

- 1196 NAKAJIMA T., KAKUWA Y., YASUDOMI Y., ITAKI T., MOTOYAMA I., TOMIYAMA T.,
- 1197 MACHIYAMA H., KATAYAMA H., OKITSU O., MORITA S., TANAHASHI M. & MATSUMOTO R.
- 1198 (2014). Formation of pockmarks and submarine canyons associated with dissociation of gas
- 1199 hydrates on the Joetsu Knoll, eastern margin of the Sea of Japan. Journal of Asian Earth
- 1200 Sciences, **90**, 228-242.
- 1201 OLU K., CAPRAIS J.C., GALERON J., CAUSSE R., VON COSEL R., BUDZINSKI H., ... & SIBUET M.
- 1202 (2009). Influence of seep emission on the non-symbiont-bearing fauna and vagrant species
- 1203 at an active giant pockmark in the Gulf of Guinea (Congo–Angola margin). Deep Sea
- 1204 *Research Part II: Topical Studies in Oceanography*, **56**, 23, 2380-2393.
- 1205 ONDREAS H., OLU K., FOUQUET Y., CHARLOU J.L., GAY A., DENNIELOU B., ... & SIBUET M.
- 1206 (2005). Integrated "in situ" study of a deep giant pockmark on the Congo-Angola margin. -
- 1207 *Geo-Marine Letters*, **25**, 5, 281-292.
- 1208 ORANGE D.L., ANGELL M.M. & LAPP D. (1999). Using seafloor mapping (bathymetry and
- 1209 backscatter) and high resolution sub-bottom profiling for both exploration and production:
- 1210 detecting seeps, mapping geohazards, and managing data overload with GIS. Offshore
- 1211 Technology Conference.
- 1212 OREMLAND R.S. (1979). Methanogenic activity in plankton samples and fish intestines: a
- 1213 mechanism for in situ methanogenesis in oceanic surface water. Limnol. Oceanogr. 24,
- 1214 1136-1141.
- 1215 ORPHAN V.J., HINRICHS K.U., USSLER W I.I.I., PAULL C.K., TAYLOR L.T., SYLVA S.P., ... &
- 1216 DELONG E.F. (2001). Comparative analysis of methane-oxidizing archaea and sulfate-
- 1217 reducing bacteria in anoxic marine sediments. Applied and Environmental Microbiology, 67,
- 1218 4, 1922-1934.

- 1219 OSBORNE, M. J. & SWARBRICK, R. E. (1997). Mechanisms for generating overpressure in
- sedimentary basins: a reevaluation. *AAPG bulletin*, **81**, 6, 1023-1041.
- 1221 PAULL C.K., CHANTON J.P., NEUMANN A.C., COSTON J.A. & MARTENS C.S. (1992). -
- 1222 Indicators of methane-derived carbonates and chemosynthetic organic carbon deposits:
- 1223 examples from the Florida escarpment. In: BEAUCHAMP B. & VON BITTER P., Eds.,
- 1224 Chemosynthesis: Geological Processes and Products. Soc. Econ. Paleontol. Mineral., 361–
- 1225 375.
- 1226 PUFAHL P.K., MASLIN M.A., ANDERSON L., BRÜCHERT V., JANSEN F., LIN H., PEREZ M., VIDAL
- 1227 L. & SHIPBOARD SCIENTIFIC PARTY (1998). Lithostratigraphic summary for Leg 175: Angola-
- 1228 Benguela upwelling system. In: Proceedings Ocean Drilling Program, Initial Reports, 175, 533-
- 1229 542.
- 1230 REEBURGH W. S. (1976). Methane consumption in Cariaco Trench waters and sediments. -
- 1231 Earth and Planetary Science Letters, 28, 337-344.
- 1232 REEBURGH W.S. (1980). Anaerobic methane oxidation: rate depth distribution in Skan Bay
- sediments. *Earth and Planetary Science Letters*, **47**, 3, 345-352.
- 1234 RIBOULOT, V., SULTAN, N., IMBERT, P., & KER, S. (2016) Initiation of gas-hydrate pockmark
- in deep-water Nigeria: Geo-mechanical analysis and modeling. *Earth and Planetary Science Letters*, **434**, 252-263.
- 1237 RITGER S., CARSON B. & SUESS E. (1987). Methane-derived authigenic carbonates formed
- 1238 by subduction-induced pore water expulsion along the Oregon/Washington margin. GSA
- 1239 *bulletin*, **98**, 147-156.
- 1240 ROHLING, E.J. (2013) -Oxygen Isotope Composition of Seawater. In: Elias S.A. (ed.) The
- 1241 Encyclopedia of Quaternary Science 2, 915-922. Amsterdam: Elsevier.

- 1242 RÖMER M., SAHLING H., PAPE T., DOS SANTOS FERREIRA C., WENZHÖFER F., BOETIUS, A., &
- 1243 BOHRMANN G. (2014). Methane fluxes and carbonate deposits at a cold seep area of the
- 1244 Central Nile Deep Sea Fan, Eastern Mediterranean Sea. *Marine Geology*, **347**, 27-42.
- 1245 ROUBY D., RAILLARD S., GUILLOCHEAU F., BOUROULLEC R. & NALPAS T. (2002). Kinematics
- 1246 of a growth fault/raft system on the West African margin using 3-D restoration. *Journal of*
- 1247 Structural Geology, **24**, 783–796.
- 1248 SAHLING H., BOHRMANN G., SPIESS V., BIALAS J., BREITZKE M., IVANOV M., KASTEN S.,
- 1249 KRASTEL S. & SCHNEIDER R. (2008) Pockmarks in the Northern Congo Fan area, SW Africa:
- 1250 Complex seafloor features shaped by fluid flow. *Marine Geology*, **249**, 206-225.
- 1251 SASSEN R., MACDONALD I. R., REQUEJO A.G., GUINASSO JR N.L., KENNICUTT II M.C., SWEET
- 1252 S.T. & BROOKS J.M. (1994). Organic geochemistry of sediments from chemosynthetic
- 1253 communities, Gulf of Mexico slope. *Geo-Marine Letters*, **14**, 110-119.
- 1254 SAVINI A., MALINVERNO E., ETIOPE G., TESSAROLO C. & CORSELLI, C. (2009). Shallow seep-
- 1255 related seafloor features along the Malta plateau (Sicily channel–Mediterranean Sea):
- 1256 Morphologies and geo-environmental control of their distribution. Marine and Petroleum
- 1257 Geology, 26, 9, 1831-1848.SCRANTON M. & BREWER P.G. (1978). Consumption of dissolved
- 1258 methane in the deep ocean. *Limnol. Oceanol.*, **15**, 1978, 883–886
- 1259 SÉRANNE M., SÉGURET M. & FAUCHIER M. (1992). Seismic super-units and post-rift
- 1260 evolution of the continental passive margin of southern Gabon. Bulletin de la Société
- 1261 *Géologique de France*, **163**, 2, 135–146.
- 1262 SÉRANNE M. (1999). Early Oligocene stratigraphic turnover on the west Africa continental
- 1263 margin: a signature of the Tertiary greenhouse-to-icehouse transition? Terra Nova, 11, 135-
- 1264 140.

- 1265 SÉRIÉ C., HUUSE M. & SCHØDT N.H. (2012). Gas hydrate pingoes: Deep seafloor evidence of
- 1266 focused fluid flow on continental margins. *Geology*, **40**, 3, 207-210.
- 1267 SHIPLEY T.H., HOUSTON M.H., BUFFL ER R.T., SHAUB F.J., MCMILLEN K.J., LADD J.W. &
- 1268 WORZEL J.L. (1979) Seismic evidence for widespread possible gas hydrate horizons on
- 1269 continental slopes and rises. American Association of Petroleum Geologists Bulletin, 63,
- 1270 2204-2213.
- 1271 SIMONETTI A., KNAPP J.H., SLEEPER K., LUTKEN C.B., MACELLONI L. & KNAPP C.C. (2013). -
- 1272 Spatial distribution of gas hydrates from high-resolution seismic and core data, Woolsey
- 1273 Mound, Northern Gulf of Mexico. *Marine and Petroleum Geology*, **44**, 21-33.
- 1274 SLOAN E.D. & KOH C.A (2007) Clathrate Hydrates of Natural Gases. Third Edition, CRC
- 1275 Press., 364-394.
- 1276 STAKES D.S., ORANGE D., PADUAN J.B., SALAMY K.A. & MAHER N. (1999). Cold-seeps and
- 1277 authigenic carbonate formation in Monterey Bay, California. *Marine Geology*, **159**, 1, 931278 109.
- 1279 SUESS E., TORRES M.E., BOHRMANN G., COLLIER R.W., GREINERT J., LINKE P., ... & ZULEGER
- 1280 E. (1999). Gas hydrate destabilization: enhanced dewatering, benthic material turnover and
- 1281 large methane plumes at the Cascadia convergent margin. Earth and Planetary Science
- 1282 *Letters*, **170**, 1, 1-15.
- 1283 SUJITH P.P., GONSALVES M.J.B.D., RAJKUMAR V. & SHEBA V.M. (2014). Manganese cycling
- 1284 and its implication on methane related processes in the Andaman continental slope
- sediments. *Marine and Petroleum Geology*, **58**, 254-264.
- 1286 SULTAN N., FOUCHER J.P, COCHONAT P., TONNERRE T., BOURILLET J.F., ONDREAS H.,
- 1287 CAUQUIL E. & GRAULS D. (2004). Dynamics of gas hydrate: case of the Congo continental
- 1288 slope. *Marine Geology*, **206**, 1, 1-18.

- 1289 SULTAN N., VOISSET M., MARSSET T., VERNANT A.M, CAUQUIL E., COLLIAT J.L & CURINIER V.
- 1290 (2007). Detection of free gas and gas hydrate based on 3D seismic data and cone
- penetration testing: An example from the Nigerian Continental Slope. *Marine Geology*, 240,
 1-4, 235-255.
- 1293 SULTAN N., MARSSET B., KER S., MARSSET T., VOISSET M., VERNANT A.-M., BAYON G.,
- 1294 CAUQUIL E., ADAMY J., COLLIAT J.-L. & DRAPEAU D. (2010). Hydrate dissolution as a
- 1295 potential mechanism for pockmark formation in the Niger delta. Journal of Geophysical
- 1296 Research: Solid Earth (1978–2012), **115**, B8.
- 1297 SULTAN N., BOHRMANN G., RUFFINE L., PAPE T., RIBOULOT V., COLLIAT J. L., ... & MARSSET
- 1298 T. (2014). Pockmark formation and evolution in deep water Nigeria: Rapid hydrate growth
- 1299 versus slow hydrate dissolution. *Journal of Geophysical Research: Solid Earth*, **119**, 4, 2679-
- 1300 2694.
- 1301 TRYON M.D., BROWN K.M., TORRES M.E. TRÉHU A.M., MCMANUS J. & COLLIER R.W. (1999).
- 1302 Measurements of transience and downward fluid flow near episodic methane gas vents,
- 1303 Hydrate Ridge, Cascadia. *Geology*, **27**, 12, 1075-1078.
- 1304 UCHUPI E. (1992). Angola Basin: geohistory and construction of the Continental Rise. In:
- 1305 POAG C.W. & DE GRACIANSKY P.C., Eds., Geologic Evolution of Atlantic Continental Rises. -
- 1306 Van Nostrain Reinhold, New York, 77–99.
- 1307 UENZELMANN-NEBEN G. (1998). Neogene sedimentation history of the Congo Fan. -
- 1308 *Marine and Petroleum Geology*, **15**, 635–650.
- 1309 USSLER III W. & PAULL C.K. (1995). Effects of ion exclusion and isotopic fractionation on
- 1310 pore water geochemistry during gas hydrate formation and decomposition. Geo-Marine
- 1311 *Letters,* **15**, 1, 37-44.

- 1312 VALENTINE D.L. & REEBURGH W.S. (2000). New perspectives on anaerobic methane
- 1313 oxidation. *Environmental Microbiology*, **2**, 5, 477-484.
- 1314 VALLE P.J., GJELBERG J.G., HELLAND-HANSEN W. (2001). Tectonostratigraphic development
- 1315 in the eastern Lower Congo Basin, offshore Angola, West Africa. Marine and Petroleum
- 1316 *Geology*, **18**, 909-927.
- 1317 WEI J., PAPE T., SULTAN N., COLLIAT J.-L., HIMMLER T., RUFFINE L., DE PRUNELE A.,
- 1318 DENNIELOU B., GARZIGLIA S., MARSSET T., PETERS C.A., RABIU A., BOHRMANN G. (2015). -
- 1319 Gas hydrate distributions in sediments of pockmarks from the Nigerian margin Results and
- 1320 interpretation from shallow drilling. *Marine and Petroleum Geology*, **59**, 359-370.
- 1321 WHITICAR M. J. (1999). Carbon and hydrogen isotope systematics of bacterial formation
- and oxidation of methane. *Chemical Geology*, **161**, 1, 291-314.
- 1323 YADAV D.N. (1996). Manganese mobilization from the western continental margin of India.
- 1324 Current Science-Bangalore, **71**, 900-905.
- 1325 ZACHOS J., PAGANI M., SLOAN L., THOMAS E. & BILLUPS K. (2001). Trends, rhythms, and
- aberrations in global climate 65 Ma to Present. *Science*, **292**, 686–693.

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Fig.1: Bathymetric map of the Lower Congo Basin from EM12 multibeam acquisition (Zaïango project, 1998-2000) showing the location of the study area, on the upper part of the slope.

Fig. 2: Regional geoseismic section across the West African Margin illustrating the general
 stratigraphic architecture and salt tectonics (location on Fig. 1), modified from Babonneau *et al.*, 2002.

Fig.3: A. Two-way time map of the seafloor with dip overlain showing the 2D and 3D seismic coverage and the area covered by side-scan sonar (red rectangle). **B.** Bathymetric map of the area of interest with the two ROV tracks (orange and purple) and the two sites where carbonates were sampled.

1344 Fig.4: A. Bathymetric map of the seafloor showing Morphotype A which is characterized by a 1345 smooth and regular morphology; Morphotype B, which is rougher and slightly depressed and 1346 Morphotype C, which consists of elongate depressions. B. Color-coded dip of the seabed 1347 calculated from the 3D two-way time map of the seafloor. Both Morphotype A and Morphotype B just show the regional dip, while Morphotype C is marked by high dips that 1348 1349 correspond to the margins of the elongated depressions. C. Seabed reflectivity from the side 1350 scan sonar data showing Morphotype A and B with a low reflectivity, whereas Morphotype C 1351 is strongly reflective, indicating a higher acoustic impedance. Reflectivity highlights a series 1352 of elliptical patches that develop along the depressions of Morphotype C. D. Coherency map of the seabed from 3D seismic data highlighting the difference between Morphotype A 1353 1354 (highest coherency), Morphotype B with an intermediate coherency (especially in the NW 1355 patch) and Morphotype C, with a very low coherency.

Fig.5: Morphotypes distribution from the compilation of the maps of Fig. 5. This compositemap highlights the presence of two similar structures, each composed of a subcircular patch

of Morphotype B with a set of peripheral elongated depressions (Morphotype C) dominantlyextending to the SE of the patch.

1360 Fig.6: A. Map of the seabed reflectivity showing the two spiders structures (SS1 and SS2), 1361 the major normal faults and the location of the 2 seismic lines AB and CD. B. Isopach map of 1362 the interval between the seafloor and the BSR, showing that the BSR is distributed in two 1363 patches and that it is shallower in the SE than in the NE. C. Seismic section AB (see Fig.3 for location) from the HR 3D volume, showing the two tilted BSRs associated with a strong 1364 amplitude decrease and a distortion of reflections underneath. The seabed shows an 1365 1366 asymmetrical "red over black" signal, meaning that the seismic is not zero-phase [Brown, 1367 2011]; conversely, the BSRs appear as "black over red", i.e. with the opposite polarity. The 1368 set of high amplitudes at depth is known to correspond to hydrocarbon-bearing reservoirs. 1369 D. Seismic section CD (see Fig.5.A for location) showing the tilted BSR and its 1370 correspondence with each morphotypes A, B and C at the seafloor.

Fig.7: Gas hydrates stability diagram for both pure methane and different proportions of methane (methane + ethane mixture) [from Sloan and Koh, 2007] on which are plotted several couples of temperature/pressure points corresponding to the observed patches of BSR. Calculation of the temperature at the BSR was made with 3 geothermal gradients obtained close to the structure of interest [Sultan *et al.*, 2004].

Fig.8: Seismic sections (location shown on figure 5) across the main patch of Morphotype B. **A.** Insert from 3D seismic data to show the context above the BSR. **B.** Close-up of the zone shown on A with a white rectangle on 2D-AUV data (envelope display, see text). This highresolution display highlights the gentle depression associated with Morphotype B, and shows 4 levels of discontinuous sets of aligned reflections underneath, vertically spaced by 10 to 20 ms. The signal labeled "direct arrival" at the top is a seismic acquisition artifact and

1382 not a geological reflection. C. Amplitude display of the same seismic profile as B over the SW 1383 margin of the depression showing reflection geometry down to below level 1. Seven 1384 horizons have been picked and show downwarping below the margin of the depression. The 1385 two vertical seismic profiles show the exact location of the rim of the depression (left) and 1386 its lowest point (right). The highest point of the picked horizons is not perfectly aligned with 1387 the rim, showing that these horizons are not multiples. A number of diffraction hyperbolae 1388 can be seen (white circles) where the aligned reflections were observed on 7B. They all show 1389 the same curvature, idealized in the box labeled "DH". The curvature of the NE edges of the 1390 picked horizons is much gentler, indicating that the reflections correspond to the presence 1391 and morphology of real reflectors in subsurface. Vertical scale is in seconds TWT.

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Fig.9: A. Seismic section from 3D seismic data for the context (location shown on Fig.5) across the elongated depressions of Morphotype C, shown in a white rectangle. **B.** Section from 2D-AUV seismic data (envelope display). The seismic profile shows high-amplitude anomalies below each of the depressions, with the deepest anomaly below the gentlest surface depression.

1398 Fig.10: Seafloor pictures from submersible dives, taken on three sites of Morphotypes B and 1399 C (locations shown on Fig.3). A. Bacterial mats (white patches) associated with black reduced 1400 sediments and empty shells of bivalves. B. Accumulation of empty bivalve shells scattered on 1401 hemipelagic sediments. C. Small mount formed by carbonate tubes popping through soft 1402 mud. D. Flat-topped carbonate crust with a conical shape emerging from the mud, which is 1403 highly broken, and crabs walking over. E. Flat-topped 'tabular carbonate crust', showing a 1404 high porosity with living tubeworms and crabs. F. Scrappy carbonate crust with white 1405 bacterial mats associated with black reduced sediments in between.

Fig. 11: Carbonate samples recovered from sites 2 (A, B, D) and 3 (C). **A.** Shell fragments, very heterogeneous in size, poorly cemented and showing a very high porosity. **B**. Section through a tubular carbonate showing the presence of a central conduit connected to peripheral conduits of smaller diameter. **C**. Crumbly carbonate made of cemented shell fragments with a high porosity. **D**. Well indurated tubular carbonate.

Fig.12: Geochemical data. A. Concentrations of dissolved methane, iron and manganese
measure: very close to the seabed, along the ROV track over Morphotypes A, B and C.
Bathymetry in background. B. Vertical evolution of iron and manganese concentrations in
the water column above station BZR01 (location on Fig. 3). C. Same as B for methane.

Fig.13: Distribution of carbonate samples, recovered over Morphotype C (on sites 2 and 3),
in a ¹³C vs. ¹⁶D diagram showing the possible sources of carbon [modified from Campbell,
200].)

1418 Fig.14: Schematic evolution of the Spider Structures in relationship with a cycle of methane 1419 input linked with the dynamic of the gas hydrate formation. A. (above): Incipient methane 1420 supply, the gas starts feeding the BSR but high fluxes reach the seabed and feed an active 1421 fluid vent associated with well-developed seep carbonates. B. (centre): The BSR is fully 1422 developed and plugs the porosity, so that continuously incoming methane cannot reach the 1423 seafloor as before, but it is diverted upslope and starts spilling over to the east. C. (below): 1424 As methane spills over upslope, it allows the gradual growth of the BSR upslope. Methane 1425 starts escaping to the surface making the elongated depressions of Morphotype C that 1426 correspond to the active methane venting sites.

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1429	Table 1 : Isotopic analysis ($\stackrel{\text{lig}}{=} c$ and $\stackrel{\text{lig}}{=} p$) made on carbonates samples recovered over
1430	Morphotype C on site 2 and 3. Samples analyzed on site 2 correspond to the cement fraction
1431	(C-c2) and the shell fraction (C-Sh2) of a carbonate sample of Fig.10.A, and an empty shell of
1432	bivalve (Sh2). The sample analyzed on site 3 corresponds to a carbonate (Carb3) of Fig.10.C.
1433	Table 2 : Concentrations of dissolved methane, iron, manganese and silica measured 1 to 2 m
1434	above the seabed along the ROV track. These concentrations have been measured at 15
1435	points in Morphotypes A, B and C, and evidence high lateral variability.
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Debth below MSL (km) 0 MSM 50 km OCEANIC CRUST Salt diapirs TRANSITIONAL CRUST Congo canyon **RIFTED CONTINENTAL CRUST** ENE 10 8 6 4 Ň Ò Miocene Oligocene Cenomanian Aptian salt layer Pre-rift Quaternary Pliocene

1461 Fig.3:



1466 Fig.4:



1479 Fig.5





1491 Fig.7:





1505 Fig.9:


1516 Fig.10:



1523 Fig.11:



1531 Fig.12:



1541 Fig.13:





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		Samples	δ ¹³ C (PDB)	δ ¹⁸ Ο (PDB)	CaCO3 (%)
		Carbonate Cement fraction (C-c2)	-35,5	4,3	75,3
	Site 2	Carbonate Shell fraction (C-Sh2)	-3,1	3,6	89,3
		Bivalve Shell (Sh2)	2,1	3,7	94,5
1 - 10	Site 3	Carbonate sample (Carb3)	-34,3	4,1	74,4
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1548 Table 1:

1566 Table 2:

A. Hydrocats BZR01 samples:																	
	Depth (m)	653	646	630	620	610	600	580	560	540	520	480	440	400	300	200	
	CH4 (nmol/l)	3,9	4,1	3,4	3,1	2,2	2,1	1,4	0,9	0,7	0,8	1	1,5	1,6	2,3	3,5	
	Fe (nmol/l)	75,1	52,8	37,7	35,3	36,1	40,9	34,5	36,1		19,3	20,1	17,8	14,6	17,8	7,4	
	Mn (nmol/l)	6,4	6,1	5,1	5,6	4,9	4,9	4,7	3,9		4,9	3,7	3,9	3,7	3,9	3,4	3

B. ROV water samples :

Num d'ech (Zaïrov)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Seismic morphotypes	MA	MA	MB	MC	MC	MC	MC	MC	MB	MC	MC	MC	MA	MA	MA
CH4 (nmol/l)		3	16	23	70	68	42	43		18	20	24	6		3
Fe(nmol/l)	309	597	278	185	287		436	867	222	265	234	188	185	188	154
Mn (nmol/l)	9	45	17	13	3		21	74	13	9	6	14	17	11	11
Si (µmol/l)	22	39	40	35	35	36	36	36	33	33	32	33	32	31	31