OCCURRENCE OF GAS HYDRATES IN SEDIMENTS IN "EMOBS" FIELDS OFFSHORE WESTERN NIGER DELTA: POCK MARKS AND SEEPAGE SITES.

ABSTRACT

6 Increased oil and gas exploration activity in the Niger Delta region of Nigeria has led to a detailed 7 investigation of the sea floor status. In this paper, we analyzed the high resolution Side scan sonar and subbottom profiler data in Niger Delta offshore basin to understand the shallow structures 8 9 and shallow deposits for gas hydrates. Observed mounds and depressions show fluid/gas migration features such as acoustic voids, acoustic chimneys, and acoustic turbid layers. Such 10 fluids are usually rich in low molecular weight hydrocarbons, mainly methane, with small amount 11 12 of other gases, such as carbon dioxide and hydrogen sulfide. Formation and decomposition of gas 13 hydrate potentially change the properties of marine sediment. In order to understand the 14 evolution and morphological changes of marine cold seeps, it is important to know the occurrence and distribution of gas hydrate in shallow sediment. Gas enclathrated in hydrate also contains 15 important information and is helpful to understand the source of the gas. There are several 16 17 implications of dynamically forming and disintegrating gas hydrate pin goes on the seafloor. The two most important ones are believed to be: For engineering and anthropogenic seabed usage, 18 i.e., seabed topography changes over time. For biology/environment, i.e., the possibility for 19 20 enhanced local primary (microbial) productivity.

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22 Keywords: gas hydrate, pockmark, sea floor, lithology, geohazards

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INTRODUCTION

Generally, analyses of the occurrence and distribution of gas hydrate deposits show that the 27 28 fluid venting areas are the potential sites (pockmarks) of gas hydrate accumulation. The areas 29 of fluid venting may be controlled by the tectonic settings of the region. For example, structures formed due to salt or shale tectonics govern the occurrence of gas hydrate in the 30 Niger Delta front. The seismic character of fluid/gas movement like acoustic voids, acoustic 31 chimneys and acoustic turbid layers have been mapped using high resolution seismic data. 32 Hydrocarbon seepages are of great significance to explorationists because they are often direct 33 34 indicators of the existence of petroleum systems (Ibe and Chuku, 2015). These processes have previously been documented in a wide variety of geological settings using highly specialized 35 underwater vehicles, cruise ships and remote satellite data. The relationship between seabed 36 morphology with shallow gas venting features are well known from Mid Norway, Nile deep-sea 37 fan, Costa Rica and Gulf of Cádiz (Hovland, 1990; Loncke, et al., 2004; Peterson, et al., 2009; 38 39 Somoza et al., 2003). Therefore, we made an attempt to analyze the seabed morphology,

40 shallow subsurface structures and shallow deposits in offshore basin using high resolution side 41 scan sonar, sub-bottom profiler (SBP) and single beam swath bathymetry data and establish a 42 link between these shallow features with known areas of gas hydrate accumulation and cold 43 seeps. The deep structure obtained from multi-channel seismic data has helped in 44 understanding the geological and tectonic control on the origin of seabed morphology and gas 45 hydrate deposits.

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48 Figure 1: Location Map of the Study Location 15km offshore Western Niger Delta Nigeria 49 (Adapted from Chuku et. al, 2015).

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GEOLOGICAL SETTING OF NIGER DELTA

The Niger Delta is situated in Gulf of Guinea on the West central Africa coast and occupies the southern part of Nigeria between latitudes 4⁰00'N and 6⁰00'N and longitudes 3⁰00'E and 9⁰00'E. It is bounded in the south by the Gulf of Guinea and in the North by older (cretaceous) tectonic elements which include the Anambra Basin, Abakiliki uplift and the Afikpo syncline. To the East and West respectively, the Niger Delta is bounded by the Cameroon volcanic line and Dahomey 58 Basin. The study area is a pockmark field as well as gas hydrates located within the Gulf of 59 Guinea on the continental margin offshore Nigeria. This continental margin is undergoing slow 60 deformation by gravity tectonism that initiated in response to both, rapid seaward 61 progradation and loading huge amount of sediment (Damuth, 1994). Distinguished this area into three subareas based on the structural styles: 1) an upper extensional 83 zone, 2) an 62 63 intermediate translational zone, and 3) a lower compressional zone. The pockmark field studied in this paper is located in the translational zone which is characterized by diapirs underneath. 64 Examples of seismic recordings of shale diapirs in this area can be found in Damuth (1994) and 65 66 Cohen and McClay (1996). The Nigerian continental margin is an active fluid flux area as indicated from various seafloor features, such as pockmarks, mud volcanoes, gas hydrates and 67 carbonate concretions (Bayon et al., 2007; Brooks et al., 2000; Graue, 2000; Hovland et al., 68 69 1997). Formation of such authigenic carbonates is typically attributed to the anaerobic methane 70 oxidation. Pronounced bottom simulating reflectors (BSR), demonstrating the boundary 71 between the base of the free gas underneath, were reported. Such BSRs indicate the presence 72 of gas hydrates related to high methane flux towards shallow sediments caused by fluid migration. In addition, gas chimneys found in the subsurface were proposed to serve as 73 74 pathways for fast hydrocarbon migration between reservoirs and the seafloor (Heggland, 75 2003). The pockmark field, comprising the pockmarks A and C studied herein, lies at water 76 depths between 15m and 19m. Pockmark A is a slightly NE-SW elongated seafloor feature with 77 a hummocky topography in the center. The hummocky area corresponds to high singlebeam 78 backscatter which may indicate the occurrence of shallow gas hydrates, free gas and/or 79 authigenic carbonates.

80 FORMATION OF GAS HYDRATES

81 (Gas hydrates are ice-like substances that form in deep-sea sediments)

UNDER PEER REVIEW



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Figure 2 An aggregation of methane ice worms inhabiting a white methane hydrate seen in the Gulf of Mexico, 2102. Studies suggest that these worms eat chemoautotrophic bacteria that are

85 living off of chemicals in the hydrate. *Image courtesy of NOAA Okeanos Explorer Program*.

86 When gas molecules are trapped in a lattice of water molecules at temperatures above 0°C and pressures above one atmosphere, they can form a stable solid. These solids are gas hydrates. 87 Most gas hydrates are formed from methane (CH4). Methane is the simplest hydrocarbon, and 88 is the primary component of the natural gas that we burn for energy. If you hold a hydrate 89 nodule in your hand and light it with a match, it will burn like a lantern wick. There is fire in this 90 ice! Gas hydrate deposits along ocean margins are estimated to exceed known petroleum 91 reserves by about a factor of three. These hydrate beds leak gases into the water, forming cold 92 93 seeps on the ocean floor. This hydrocarbon seepage is common on continental margins around the world. Chemosynthetic communities similar to those found at hydrothermal vents form at 94 cold seeps, using hydrocarbons or hydrogen sulfide for carbon and energy. Seep tube worms, 95 96 mussels, and clams form two-meter-high bushes over kilometer-sized beds. Most seeps are also 97 characterized by high microbial productivity. Hydrates influence ocean carbon cycling, global 98 climate change, and coastal sediment stability. Localized meltdowns have caused massive 99 continental slope failure, which can present a geological hazard for shelf oil and gas production. Massive hydrate dissolution events, releasing vast amounts of the greenhouse gas methane, 100

are possible causes of some of the abrupt climate changes seen in the geologic record. 101 102 Methane hydrates (or gas hydrates) are cage-like lattices of water molecules containing 103 methane, the chief constituent of natural gas. They may represent one of the world's largest 104 reservoirs of carbon-based fuel. However, with abundant availability of natural gas from conventional and shale resources, there is no economic incentive to develop gas hydrate 105 106 resources, and no commercial-scale technologies to exploit them have been demonstrated. Gas 107 hydrates can be found under arctic permafrost, as well as beneath the ocean floor. They can also form during drilling and production operations. So far, gas hydrates have provided more 108 109 problems than solutions. The formation of gas hydrates in deepwater production can hinder operations; managing or preventing their formation in deepwater oil and gas wells and 110 pipelines has been a challenge for many decades, and addressing the existence of gas hydrates 111 112 is a major part of planning for deepwater drilling and production. However, at some point in the future, gas hydrates could be a potential source of natural gas. When brought back to the 113 114 earth's surface, one cubic foot of gas hydrate releases 164 cubic feet of natural gas. According 115 to the United States Geological Survey, the world's gas hydrates may contain more organic carbon than the world's coal, oil, and other forms of natural gas combined. Estimates of the 116 117 naturally occurring gas hydrate resource vary from 10,000 trillion cubic feet to more than 100,000 trillion cubic feet of natural gas. Tapping such resources would require significant 118 119 additional research and technological improvements.

- 120 Gas hydrates are of great importance for a variety of reasons. In offshore hydrocarbon drilling
- and production operations, gas hydrates cause major, and potentially hazardous flow assurance
- 122 problems. Naturally occurring methane clathrates are of great significance in their potential for
- as strategic energy reserve, the possibilities for CO2 disposal by sequestration, increasing
- awareness of the relationship between hydrates and subsea slope stability, the potential
- dangers posed to deepwater drilling installations, pipelines and subsea cables, and long-term
- 126 considerations with respect to hydrate stability, methane (a potent greenhouse gas) release,
- 127 and global climate change.



- 128
- 129 Figure-3 Major issues of gas hydrates.

130 HYDRATES IN OFFSHORE HYDROCARBON PRODUCTION OPERATIONS

131 DRILLING

In drilling, record water depths are continuously being set by oil companies in the search of 132 hydrocarbon reserves in deep waters. Due to environmental concerns and restrictions, water 133 based drilling fluids are often more desirable than oil based fluids, especially in offshore 134 exploration. However, a well-recognized hazard in deep water offshore drilling, using water 135 136 based fluids, is the formation of gas hydrates in the event of a gas kick. In deep-water drilling, the hydrostatic pressure of the column of drilling fluid and the relatively low seabed 137 temperature could provide suitable thermodynamic conditions for the formation of hydrates in 138 the event of a gas kick. This can cause serious well safety and control problems during the 139 containment of the kick. Hydrate formation incidents during deep-water drilling are rarely 140 reported in the literature, partly because they are not recognized. 141 142 The formation of gas hydrates in water based drilling fluids could cause problems in at least two 143 ways: Gas hydrates could form in the drill string, blow-out preventer (BOP) stack, choke and 144 • kill line. This could result in potentially hazardous conditions, i.e., flow blockage,

- kill line. This could result in potentially hazardous conditions, i.e., flow blockage,
 hindrance to drill string movement, loss of circulation, and even abandonment of the
 well.
- As gas hydrates consist of more than 85 % water, their formation could remove
 significant amounts of water from the drilling fluids, changing the properties of the fluid.

- 150 This could result in salt precipitation, an increase in fluid weight, or the formation of a 151 solid plug.
- The hydrate formation condition of a kick depends on the composition of the kick gas as well as the pressure and temperature of the system. As a rule of thumb, the inhibition
- 154 effect of a saturated saline solution would not be adequate for avoiding hydrate
- 155 formation in water depth greater than 1000 m. Therefore, a combination of salts and
- 156 chemical inhibitors, which could provide the required inhibition, could be used to avoid
- 157 hydrate formation.
- 158 PRODUCTION
- 159 The ongoing development of offshore marginal oil and gas fields increases the risks of facing
- 160 operational difficulties caused by the presence of gas hydrates. A typical area of concern is
- 161 multiphase transfer lines from well-head to the production platform where low seabed
- 162 temperatures and high operation pressures increase the risk of blockage due to gas hydrate
- 163 formation (Figure-2). Other facilities, such as wells and process equipment, can also be prone to
- 164 hydrate formation.

165 Different methods are currently in use for reducing hydrate problems in hydrocarbon transfer 166 lines and process facilities. The most practical methods are:

- At fixed pressure, operating at temperatures above the hydrate formation temperature. 167 168 This can be achieved by insulation or heating of the equipment. • At fixed temperature, operating at pressures below hydrate formation pressure. 169 170 Dehydration, i.e., reducing water concentration to an extent of avoiding hydrate formation. 171 Inhibition of the hydrate formation conditions by using chemicals such as methanol and 172 173 salts. • Changing the feed composition by reducing the hydrate forming compounds or adding 174 non hydrate forming compounds. 175 Preventing, or delaying hydrate formation by adding kinetic inhibitors. 176 •
- Preventing hydrate clustering by using hydrate growth modifiers or coating of working
 surfaces with hydrophobic substances.
- Preventing, or delaying hydrate formation by adding kinetic inhibitors.
- 180
- 181 HYDRATES IN THE NATURAL ENVIRONMENT
- 182 Hydrates as a Potential Energy Resource
- 183 Two factors make gas hydrates attractive as a potential energy resource: (1) the huge volumes
- of methane that is apparently trapped as clathrate within the upper 2000 m of the Earth's
- 185 surface, and (2) the wide geographical distribution of gas hydrates.

186 Natural gas is widely expected to be the fastest growing primary energy source in the world

187 over the next 20 years. In the U.S. Energy Information Administration's International Energy

188 Outlook 2002 (IEO2002) reference case, worldwide gas consumption is projected to almost

double to 162 trillion cubic feet in 2020 from 84 trillion cubic feet (standard conditions) in 1999.

190 Given the attractive features of gas hydrates, and the growing demand for natural gas, it seems

reasonable to conclude that gas hydrates could serve as a future energy resource.

192 A number of schemes for methane hydrate exploitation have been proposed, although at

193 present, technical and economic considerations restrict production to experimental tests only.

194 The Japan National Oil Company (JNOC) has been a pioneer in this field, having already drilled

195 experimental wells in the Mackenzie Delta of Northern Canad with ambitious plans for further

196 test wells in sediments of offshore Japan.One interesting branch of research in this area is the

197 possibility of CO2 sequestration. CO2 hydrate is thermodynamically more stable than methane

hydrate, so the possibility exists for sequestration of CO2 into existing seafloor clathrates,

199 whereby yielding methane. This process is particularly attractive, as it would act as both a

source and a sink with respect to greenhouse gas emissions.

201 HYDRATES AS A GEOHAZARD

The aspect of gas hydrates which has the biggest implications for human welfare at present is their 202 203 potential as a geohazard. Of particular concern is the danger posed to deepwater drilling and production operations, and the large body of evidence which now exists linking gas hydrates with 204 seafloor stability. With conventional oil and gas exploration extending into progressively deeper 205 206 waters, the potential hazard gas hydrates pose to operations is gaining increasing recognition. 207 Hazards can be considered as arising from two possible events: (1) the release of over-pressured gas 208 (or fluids) trapped below the zone of hydrate stability, or (2) destabilization of in-situ hydrates. The 209 presence of BSRs has previously been a cause of concern, as they could be considered evidence for 210 the existence of free gas (possibly at high-pressure) beneath. More recent analysis suggests however, that as long as excess water is present, there should not be a build-up of gas pressure 211 212 beneath. This is because, at the base of hydrate stability, the system approximates to 3-phase equilibrium, where pressure is fixed (generally at hydrostatic), and temperature occupies the 213 available degree of freedom. This means that any excess gas will be converted to hydrate, returning 214 the system to its equilibrium pressure (assuming there is no major barrier to the mass transfer of 215 salt). This case is likely to predominate in many hydrate-bearing sediments, although gas seeps and 216 217 mud volcanoes, common to thermogenic hydrate areas (e.g. Gulf of Mexico, Caspian Sea), could be 218 considered evidence for excess gas and pore-fluid pressures at shallow depths. In the absence of gas 219 traps, hydrates still pose a hazard due to their potential for destabilization. This danger is 220 particularly apparent in the case of conventional oil and gas exploration, for which drilling methods contrast quite markedly to the shallow piston-coring approach used by ODP in hydrate areas. 221

222 Conventional rotary drilling operations could cause rapid pressure, temperature or chemical

changes in the surrounding sediment. An increase in temperature could be caused by a hot drill

bit, warm drilling fluids, or later as high-temperature reservoir fluids rise through the well,

while the addition of hydrate inhibitors to drilling muds (to prevent hydrate formation in the

- well-bore or drill string in the event of a gas-kick) could change sediment pore-fluid chemistry.
- 227 Some, or all of these changes, could result in localized dissociation of gas hydrates in sediments
- surrounding wells. A similar case would apply to seafloor pipelines, where the transportation of
- 229 hot fluids could cause dissociation of hydrates in proximal sediments. In a worst-case scenario,
- clathrate dissociation could lead to catastrophic gas release, and/or destabilization of the
- 231 seafloor. The hazards associated with drilling in gas hydrate areas are exemplified by cases from
- the Alaskan Arctic, where subsurface permafrost hydrate destabilization has resulted in gas
- 233 kicks, blowouts, and even fires.

234 HYDRATES AND SEAFLOOR STABILITY

- A significant part of the gas hydrate geohazard problem is related to how they alter the physical
- properties of sediment. If no hydrate is present, fluids and gas are generally free to migrate
- 237 within the pore space of sediments. However, the growth of hydrates converts what was a
- 238 previously a liquid phase into a solid, reducing permeability, and restricting the normal
- 239 processes of sediment consolidation, fluid expulsion and cementation. These processes can be
- 240 largely stalled until the BHSZ is reached, where hydrate dissociation will occur.



- Figure 4 showing a significant contrast between high amplitude chaotic facies from the central
- part of the pockmark and the low-amplitude sub parallel reflectors of the surroundingsediments.
- 245
- 246 Dissociation of hydrates can arise through an increase in temperature due to increasing burial
- 247 depth (assuming continued sedimentation) or an increase in sea bottom-water temperatures,
- and/or a decrease in pressure (e.g., lowering of sea level). Upon dissociation, what was once
- solid hydrate will become liquid water and gas. This could lead to increased pore-fluid pressures

- in under-consolidated sediments, with a reduced cohesive strength compared to overlying
- 251 hydrate-bearing sediments, forming a zone of weakness. This zone of weakness could act as a
- site of failure in the event of increased gravitational loading or seismic activity. The link
- 253 between seafloor failure and gas hydrate destabilization is a well established phenomenon,
- 254 particularly in relation to previous glacial-interglacial eustatic sea-level changes. Slope failure
- can be considered to pose a significant hazard to underwater installations, pipelines and cables,
- and, in extreme cases, to coastal populations through the generation of tsunamis.



Figure-5 Potential scenario whereby dissociation of gas hydrates may give rise to subsea slope failure and massive methane gas release

260 HYDRATES AND GLOBAL CLIMATE CHANGE

Methane is a particularly strong greenhouse gas, being ten times more potent than carbon 261 dioxide. Increasing evidence points to the periodic massive release of methane into the 262 263 atmosphere over geological timescales. However, whether such enormous releases of methane are a cause or an effect with respect to global climate changes remains the subject of much 264 debate. Global warming may cause hydrate destabilsation and gas release through a rise in 265 266 ocean bottom water temperatures. Methane release in turn would be expected to accelerate warming, causing further dissociation, potentially resulting in runaway global warming. 267 However, conversely, sea level rise during warm periods may act to stabilize hydrates by 268 269 increasing hydrostatic pressure, acting as a check on warming.

270 A further possibility is that hydrate dissociation may act as a check on glaciations, whereby

reduced sea levels (due to the growth of ice sheets) may cause seafloor hydrate dissociation,

releasing methane and warming the climate. The strong link between naturally occurring gas

- 273 hydrates and the Earth's climate is an increasingly recognized phenomenon. However, there is
- still little understanding concerning the exact role gas hydrates play in global climate change.
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276 Gas hydrates (or gas clathrates) are non-stoichiometric crystalline solids comprised of

- 277 hydrocarbon gases trapped within the cavities of a rigid "cage-like" lattice of water
- 278 molecules. These compounds contain clusters (two or more) of gas-trapping polyhedra
- 279 formed by pentagonally and hexagonally arranged hydrogen-bonded water molecules.
- 280 Van der Waals interactions between the trapped (enclathrated) "guest" molecule and
- the surrounding water cage walls stabilize and support the individual polyhedra forming the
- 282 hydrate lattice and restrict the translational motion of the guest molecule.

283 Hydrate structures are classified into three categories based on the geometries of their

- 284 constituent water cages: cubic structures I and II and hexagonal structure H. Each crystalline
- structure contains geometrically distinct water cages with different size cavities which typically
- accommodate only one guest molecule ranging in diameter from 0.40 0.90 nm. [2] Structure I
- (sl) hydrates are the most commonly encountered naturally occurring hydrate structure which
- encases small diameter molecules (0.40 0.55 nm) such as methane or ethane gas. [2]
- 289 Structures II (sII) and H (sH) hydrates accomodate larger guest molecules, typically propane or
- iso-butane for sII or combinations of methane gas and nexohexane or cycloheptane, but are
 less prevalent in nature. For sI hydrates, the unit cell consists of 46 water molecules arranged
- into two small dodecahedral cages (each with twelve pentagonal faces) and six large
- tetradecahedral cages (each with two hexagonal and twelve pentagonal faces) Assuming full
- 294 occupancy, the ideal molar guest to water ratio for an sl hydrate is 1:5.75
- 295 Gas hydrates form in high pressure, low temperature environments where sufficient gas and 296 water are present. The hydrate formation requirements restrict the occurrence of natural gas 297 hydrates to two types of geologic locations: i) under permafrost in the polar continental shelves and ii) in sediment beneath the ocean floor The blue sections in the generic curves illustrate 298 regions in permafrost and oceanic sediment where the pressure and temperature conditions 299 300 and the concentration of methane gas are within the hydrate formation and stability zone. 301 These curves are based on pressure-temperature phase equilibrium data and correspond with 302 reflection seismic data collected in these environments. While several different models have 303 been developed to describe the mechanisms involved in gas hydrate formation, there is a 304 general consensus that the origin of the methane concentrated in naturally occurring hydrates is either microbial (generated by anaerobic decomposition of organic matter) or thermogenic 305 306 (generated by thermal decomposition of organic matter).
- Reflection seismology and recovered core samples are primarily used to estimate methane hydrate reserves. While core samples provide direct evidence for hydrates, they are often

- 309 difficult to obtain from regions with hydrate favorable conditions. Conversely, reflection
- seismology is routinely used as an indirect method to detect hydrate deposits in the Earth's
- 311 subsurface. This exploration technique monitors changes in the velocities of reflected seismic
- 312 waves to indicate transitions between materials with different densities. The locations of
- 313 methane hydrate deposits are inferred by identifying bottom simulating reflectors (BSRs) on the
- seismic profiles. BSRs are interpreted as the boundary between hydrate and free gas regions in
- the subsurface. In general, estimates based strictly on BSRs are considered speculative since
 hydrate bearing sediment has been extracted from regions without BSRs and vice versa.
- hydrate bearing sediment has been extracted from regions without BSRs and vice versa.
 Therefore, estimates of the global accumulations of methane hydrates vary over three orders of
- magnitude $(0.15 \times 10^{15} 3.05 \times 10^{18} \text{ m}^3 \text{ of methane at STP})$. However, even conservative
- estimates indicate that a significant amount of methane gas is concentrated in the shallow
- 320 geosphere.

Despite the relative magnitude and global pervasiveness of gas hydrate deposits, the existence of naturally occurring gas hydrates was first recognized in 1965 when a Soviet oil crew located a reservoir of methane hydrates while drilling in Siberia. [11] Prior to this discovery, gas hydrates were only known to occur in the laboratory and within the thermodynamically favorable conditions found in oil pipelines.

Since this discovery, gas hydrates have attracted interest as a potential energy resource.

321 STRATIGRAPHIC-TYPE SEDIMENTARY HYDRATE DEPOSITS

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The most common hydrate deposits on Earth are in the ocean, and are the product of largely one-dimensional processes of organic carbon burial, bacterial methanogenesis, and methane transport in slow fluid flow. Following the terminology of Milkov and Sassen (2002), we will refer to these as stratigraphic-type hydrate deposits.

327 In the steady state, the maximum concentration of hydrate is found at the base of the stability 328 zone, with bubbles found below (Davie and Buffett, 2001). Typical concentrations of hydrate are a few percent of pore volume, and the amount of bubbles below the stability zone is also a 329 few percent by volume. The layer of bubbles is clearly apparent in seismic sections of the 330 331 subsurface sediment. Temperature contours within the sediment column tend to parallel the sea floor, and so the layer of bubbles tends to parallel the sea floor as well. Stability zone is 332 referred to as a "bottom simulating reflector" or BSR. Because it is remotely detectable, the 333 334 distribution of the BSR is one of the best indications of the distribution of hydrates in 335 sediments. Most of the hydrate deposits on Earth correspond to the stratigraphic type, and 336 hence the estimates of the global inventory of hydrates are based on the physics or on the 337 observed distribution of these types of deposits. Estimates range from 500 to 10 000 Gton C as methane in hydrate globally. The estimates can be compared according to two metrics. One is 338 the area of the sea floor where hydrates can be found, and the other is the inventory of 339 340 methane, as hydrate and in some tabulation as bubbles, per square meter. Milkov (2004) does a detailed and very thorough comparison of these characteristics of estimates, leaving no need 341 for more than a summary of his results here. 342

343 HYDRATES AS FOSSIL FUEL

344

345 Another pathway by which hydrate carbon might reach the atmosphere to affect climate is if it is combusted as a fossil fuel. Estimates of the total inventory of methane in hydrate deposits 346 globally are very high, but probably only a small fraction of the hydrate reservoir would be 347 extractable (Milkov and Sassen, 2002). The largest methane reservoir, the stratigraphic 348 disseminated deposit, is the least attractive economically. The concentration of methane is 349 generally too low for economical extraction using current technology. The sediments of the 350 351 Blake Ridge are impermeable (Kvenvolden, 1999), making extraction even more unlikely, while sediments in the Nankai Trough are more permeable and hence easier to extract (Milkov and 352 Sassen, 2002), which the Japanese intend to do (Kerr, 2004). The other class of oceanic deposits 353 354 is the structurally-focused deposits, such as found in the Gulf of Mexico (Milkov and Sassen, 355 2001) and mud volcanoes (Milkov, 2000). Milkov and Sassen (2001) estimate that the Gulf of 356 Mexico contains 40 times as much hydrate methane as conventional subsurface reservoir methane in that area. 357

The most likely near-term targets for methane hydrate extraction are deposits associated with permafrost soils on land and in the shallow ocean.

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Accumulation of marine sediments in the basin probably commenced in the Albian time, after the opening of the south Atlantic ocean between the African and South American continents. Development of proto- Niger Delta, however, started only in the later Paleocene/Eocene, when sediments began to build out beyond troughs between basement horst blocks at the northern flank of the present Delta area. Since then, the delta plain has prograded southwards onto oceanic crust, gradually assuming a convex-to-the-sea-morphology (Evamy et al, 1978).

The development of the delta has been dependent on the balance between the rate of sedimentation and the rate of subsidence (Doust, Omatsola, 1990). This balance and the resulting sedimentary patterns were controlled by the structural configuration and tectonics of the basement (Evamy et al, 1978).

373

THE GEOLOGY OF GAS HYDRATE

374 375

The majority of the hydrate deposits on Earth are composed of biogenic methane, as indicated 376 377 by its isotopic composition and the lack of other short hydrocarbons such as ethane. Most of the organic matter raining to the sea floor decomposes in the top few centimeters of the 378 sediment, called the zone of early diagenesis. However, the production of methane from this 379 decaying organic matter is usually inhibited by the presence of dissolved sulfate, providing a 380 more energetically favorable respiration pathway. Sulfate is removed from pore waters deeper 381 in the sediment by reaction with methane (anaerobic oxidation of methane, AOM, described 382 above). This reaction prevents sulfate and methane from coexisting at high concentrations in 383

384 sediment pore waters. Typically both species diffuse toward their mutual annihilation at a welldefined methane/sulfate boundary (Borowski et al., 1996, 1999; D'Hondt et al., 2004). After the 385 386 depletion of sulfate, methane can be produced from solid organic carbon or by reaction of dissolved organic carbon, notably acetate, carried into the methanogenesis zone by diffusion or 387 pore water advection. Wellsbury et al. (1997) found that heating sediment in the lab, up to 388 389 60 C, stimulates the bacterial production of acetate. At Blake Ridge, the concentration of acetate reaches very high concentrations, supplying 10% of the reduced carbon necessary for 390 methane production (Egeberg and Barth, 1998). Bacterial abundances and metabolic rates of 391 392 methanogenesis, acetate formation, and AOM are extremely high at the base of the hydrate 393 and gas zone, rivaling metabolic rates at the sediment surface (Parkes et al., 2000). Bacterial activity is detected within the hydrate zone as well (Orcutt et al., 2004). 394

- 395
- 396 MATERIALS

397 Side scan sonar, subbottom profiler and echo sounder track lines (24) and sea bed samples 398 were collected in the study area in cruises.

Approximately 27 linear kilometers of side scan sonar and echo sunder data were surveyed using Geo acoustics SSS 941 Tow fish and EA 400 single beam hydrographic echo sounder.

The accurate positioning of the side-scan sonar, subbottom profiler and echo sounder track 401 402 lines was accomplished by means of a kongsberg sea path 330 receiver(DGPS). The backscatter of the surface sediments (side- scan sonar), coupled with sea bed sample has enabled the 403 distinction of the sea floor pockmarks, gas hydrates and depressions. Water depths measured 404 405 form echo sounders were used to determine the bathymetric classification and location of the study area within the inner shelf environment of the Niger Delta. Bed forms captured from the 406 407 sea bed scan were matched with the topographical features to deduce the processes shaping 408 the sea floor environment of the study area. the hypotenuse.

409



415 Figure 6: Target height measurements above sea bed.



418 Figure 7: Work flow chart

422 RESULTS

423 These consist basically of two sets of data: sub bottom data and side scan data with respect to

- lithology, pockmarks, sea floor topography, and subsurface stratigraphy and environment of
- 425 deposition.
- 426
- 427 Water Depth:

The water depth measured over the study area ranges between 15.7 to 18.3m. The shallowest water depth (15.7m) occurred in south western portion. This bathymetric range indicates that the study area is located within the middle to upper shore face setting of the inner shelf.

- 431
- 432 Lithology
- The side-scan imagery revealed low intensity back scatter dominates the entire study area. This is interpreted as clay and silt with pockets of sand.
- 435
- 436 Pockmarks
- 437 Fluid escape features such as pockmarks which are often associated with gas hydrate and
- 438 biogenic gas bearing sediments in continental margin settings were observed in the study area.
- 439 Pockmarks are seabed culminations of fluid/gas escape chimneys which appear as cone-shaped
- 440 circular or elliptical depressions.
- 441

442 SUB BOTTOM PROFILE

The seismic record of the survey area suggests the presence of the lithified sediments at approximately 20.0m to 25.0m below the sea bed. The prominent seismic stratigraphic interface that separates the lithified sediments from the overlying sea bed sediments was found to shoal towards north east of the survey corridor.







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Figure 10. Pockmarks characterized by a reflection free transparent zone to very low amplitude

453 chaotic facies and shallow heterogeneous high amplitude chaotic facies



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Figure 11 Pockmark is characterized by a reflection-free transparent zone to very low amplitude chaotic facies are projected onto the profile. For shaded areas correspond to hemipelagic

458 sediments, while the blue areas correspond to suspected gas hydrates.

UNDER PEER REVIEW



460

- 461 Figure 12 pockmark showing a significant contrast between high amplitude chaotic facies from
- the central part of the pockmark and the low amplitude subparallel reflectors of the
- 463 surrounding sediments and are projected onto the profile locations, shaded areas correspond
- 464 to hemipelagic sediments, while the blue areas correspond to suspected gas hydrates.



- 466 Figure 13. Pockmark A showing once again a significant contrast between high-amplitude
- 467 chaotic facies from the central part of the pockmark and the much more continuous seismic
- 468 facies of the surrounding sediment are projected onto the profile. Shaded areas correspond to
- 469 hemipelagic sediments, while the blue areas correspond to suspected gas hydrates.
- 470

UNDER PEER REVIEW



- 473 Figure 14. Iso diffusivity and iso-excess pore pressure contours at calculation step of 4000 years
- 474 for four different case studies: (a and e) case 1 with an initial hydrate fraction lower than the
- 475 reference
- 476
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- One presented with a hydraulic diffusivity of the hydrate phase higher
- than the one used with a heterogeneous initial hydrate fraction distribution, and value equal to
- 20 instead of the b value of 50 used in the reference calculation















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495 DISCUSSION

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497 Gas hydrate has been commonly found in sediments at the floor or at shallow depth below the seabed of pockmarks located in the hydrate stability zone of continental slopes, but the role of 498 gas hydrate in the dynamics of formation of pockmarks remain questioned. Pockmarks 499 associated with gas (free or dissolved) and gas hydrates are important globally. To assess the 500 methane release from the seabed to the ocean and ultimately to the atmosphere in climatic 501 studies investigating methane as a green house gas [Badr et al., 1991], because methane 502 503 emissions from pockmarks are a driving force of cold seep ecosystems hosting unique biota 504 [Foucher et al., 2009], and because pockmarks are often found in continental slope areas of 505 fluid driven sedimentary failure of concern to the deep offshore industry.

506 The Niger delta is areas where many seep related seabed features have been found over the last years in particular during industry exploration mapping at water depths between 500 and 507 1500 m [Hovland et al., 1997; Brooks et al., 2000; Georges and Cauquil, 2007]. Various studies 508 509 from the Nigerian continental slope have shown different seafloor sedimentary features such as pockmarks, gas hydrates, slides, mud volcanoes, and carbonate buildups associated with fluid 510 flow [Damuth, 1994; Cohen and McClay, 1996; Brooks et al., 2000; Haskell et al., 1999; Hovland 511 512 et al., 1997; Deptuck et al., 2003, among others]. Heggland [2003] observed gas chimneys above hydrocarbon charged reservoirs. These chimneys are believed to result from hydrocarbon 513 514 dysmigration (leakage of petroleum from a trap) along fault planes between source rocks of 515 reservoirs and the seabed. All these observations make the Niger delta a prime interest target to study the active interplay of fluid flow processes, gas hydrate dynamics, and seafloor 516

517 deformation. In this work we focus on a specific area, where very high resolution bathymetry data (autonomous underwater vehicles, or AUV, data from Georges and Cauquil, 2007) 518 519 acquired recently (Figure 1) show the presence of pockmarks with different shapes and sizes. 520 Some pockmarks are associated to buried channels; others are linked to surface and subsurface faults or to the occurrence of gas hydrates. In this work, we study this last type of pockmark 521 522 where gas hydrate dynamics could play an important role in the formation and development of pockmarks. We investigate (using various methods: geophysics, geotechnics, and geology) 523 whether the shape and morphology of theses pockmarks could be controlled by gas hydrate 524 525 dynamics. Finally, we use numerical modeling to validate assumptions and working hypothesis about the possible link between pockmarks formation and evolution and gas hydrate 526 dissolution processes. The investigated area which is characterized by numerous circular to sub 527 528 circular features lies at water depths ranging from 15 to 18m and is located in the transitional 529 detachment zone.

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531 532 CONCLUSION

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534 This work is the first one to show pockmarks at different stages of maturation based on seafloor and sub seafloor geophysical data in a relatively localized zone. The SBP profiles show a 535 common internal architecture of the studied pockmarks associated to gas hydrate dynamics: 536 537 sediments rich in gas hydrate at the central part of the pockmark surrounded by over pressured sediments. The temperature, pressure, and salinity conditions of the studied area demonstrate 538 that sediment deformation linked to the gas hydrate dynamics occurs in the hydrate stability 539 zone. Moreover and based on 3D seismic data and the pseudo 3D micro seismic cube, the 540 541 sediment deformations (ring shape surrounding the central part of the pockmark seem to be localized in the upper sedimentary layers and are not a direct consequence of deep depressions 542 (Figure 19). Modeling results show that the dynamic of the gas flow through faults is the main 543 cause of the hydrate dissolution and as Rehder et al. [2004] observed the long term survival of 544 gas hydrate must be sustained by sufficient supply of gas dissolution generates excess pore 545 pressure due to the compaction of the hydrated sediments. The fluid flow generated by the 546 excess pore pressure gets around the gas hydrate bearing sediment because of the low 547 548 permeability of the medium. The loss of the massive hydrate by dissolution at the boundary of the study area and the pore pressure dissipation are accompanied by sediment fracturing 549 surrounding the sediment hosted gas hydrates. 550

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