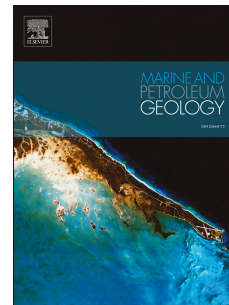


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Hydrate occurrence in Europe: A review of available evidence

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1
2 Hydrate occurrence in Europe: a review of available evidence
3

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56 Abstract

57 Large national programs in the United States and several Asian countries have defined and
58 characterised their marine methane hydrate occurrences in some detail, but European hydrate
59 occurrence has received less attention. The European Union-funded project “Marine gas hydrate – an
60 indigenous resource of natural gas for Europe” (MIGRATE) aimed to determine the European
61 potential inventory of exploitable gas hydrate, to assess current technologies for their production, and
62 to evaluate the associated risks. We present a synthesis of results from a MIGRATE working group
63 that focused on the definition and assessment of hydrate in Europe. Our review includes the western
64 and eastern margins of Greenland, the Barents Sea and onshore and offshore Svalbard, the Atlantic
65 margin of Europe, extending south to the northwestern margin of Morocco, the Mediterranean Sea,
66 the Sea of Marmara, and the western and southern margins of the Black Sea. We have not attempted
67 to cover the high Arctic, the Russian, Ukrainian and Georgian sectors of the Black Sea, or overseas
68 territories of European nations. Following a formalised process, we defined a range of indicators of
69 hydrate presence based on geophysical, geochemical and geological data. Our study was framed by
70 the constraint of the hydrate stability field in European seas. Direct hydrate indicators included
71 sampling of hydrate; the presence of bottom simulating reflectors in seismic reflection profiles; gas
72 seepage into the ocean; and chlorinity anomalies in sediment cores. Indirect indicators included
73 geophysical survey evidence for seismic velocity and/or resistivity anomalies, seismic reflectivity
74 anomalies or subsurface gas escape structures; various seabed features associated with gas escape, and
75 the presence of an underlying conventional petroleum system. We used these indicators to develop a
76 database of hydrate occurrence across Europe. We identified a series of regions where there is
77 substantial evidence for hydrate occurrence (some areas offshore Greenland, offshore west Svalbard,
78 the Barents Sea, the mid-Norwegian margin, the Gulf of Cadiz, parts of the eastern Mediterranean, the
79 Sea of Marmara and the Black Sea) and regions where the evidence is more tenuous (other areas
80 offshore Greenland and of the eastern Mediterranean, onshore Svalbard, offshore Ireland and offshore
81 northwest Iberia). We provide an overview of the evidence for hydrate occurrence in each of these
82 regions. We conclude that around Europe, areas with strong evidence for the presence of hydrate
83 commonly coincide with conventional thermogenic hydrocarbon provinces.

84

85 *Keywords:* methane hydrate; Europe

86

87 1. Introduction

88 Gas hydrate is an ice-like, crystalline solid comprising a hydrogen-bonded water lattice with trapped
89 gas molecules that is stable at high pressures and low temperatures (e.g., Sloan and Koh, 2008). In
90 nature the most common hydrate-forming gas is methane. Methane hydrate is widespread in seafloor
91 sediments and as such may provide a useful energy resource. Because, for equivalent energy
92 production, burning methane generates significantly less greenhouse gases than burning coal, the

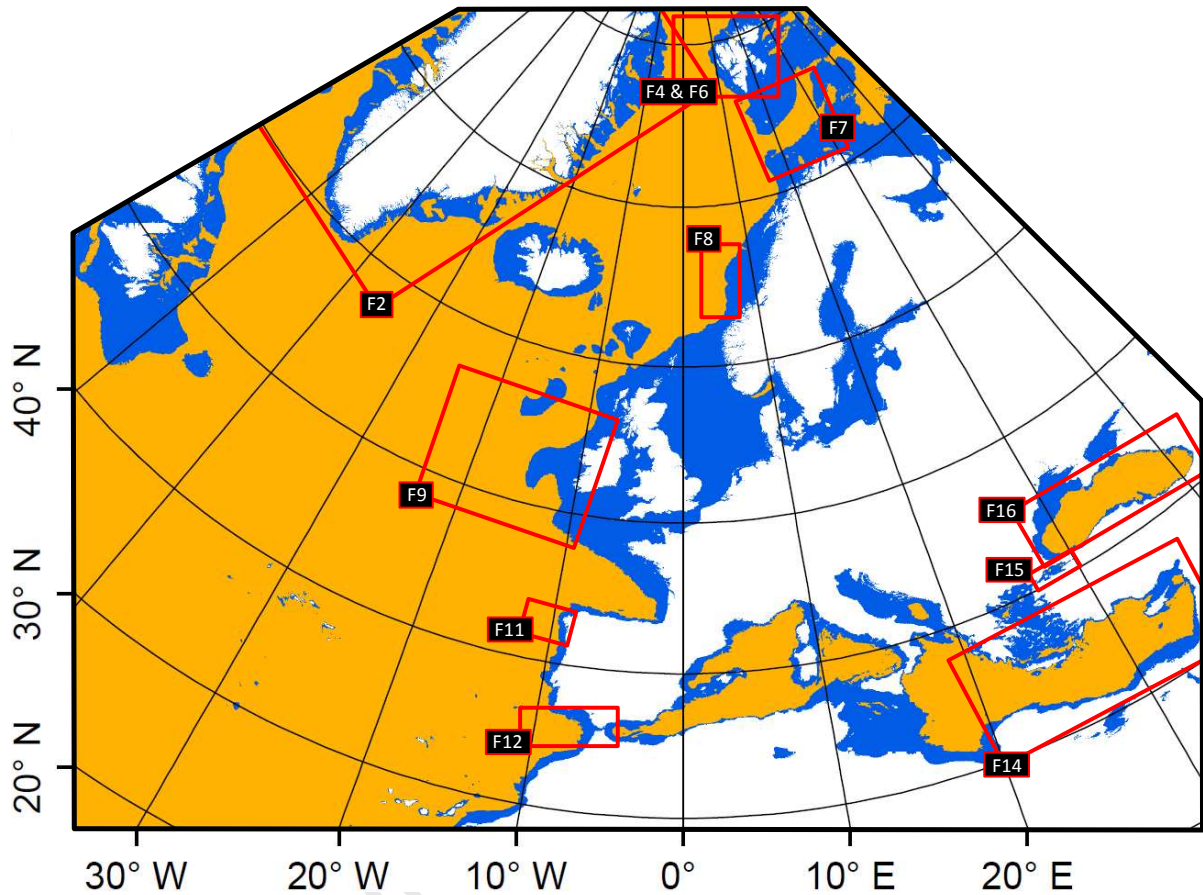
93 energy mix required to satisfy the target of keeping the average global temperature rise below 2°C
94 during the 21st century may involve substantial gas production, including from undiscovered sources
95 (e.g., McGlade and Ekins, 2015). Methane hydrate could be one such source, providing a transition
96 fuel to a low-carbon energy system that compliments intermittent renewable energy generation and
97 supports energy security. Hydrate-bearing sands have been identified as a key target for production
98 (Boswell and Collett, 2011). Hydrate is also of interest because hydrate dissociation might be
99 triggered by global ocean warming, potentially leading to further greenhouse warming (e.g., Archer et
100 al., 2009; Ruppel and Kessler, 2017), and because of their role as a potential geohazard for offshore
101 operations and infrastructure.

102
103 Driven by high demand for energy and limited conventional hydrocarbon resources, several nations,
104 including the USA, Japan, China, Korea and India, have developed large national hydrate research
105 and exploration programmes (e.g., Gabitto, 2010; Oyama and Masutani, 2017; Song et al., 2014). In
106 Europe, however, there has been less investment in hydrate research. Gas demand declined in Europe
107 during the first half of this decade, but is likely to show a modest increase in the next decade, despite
108 increasing development of renewables (Honoré, 2014). Thus there is a continuing need to better
109 understand hydrate potential in Europe, and the original motivation for this study was to provide a
110 foundation for future hydrate exploration in Europe. However, for many European nations, imported
111 shale gas is now seen as a more cost-efficient route to supplement conventional gas supplies, and
112 hydrate exploration is not seen as a priority. Therefore our study has expanded beyond a focus on
113 hydrate in sands, to cover all forms of hydrate occurrence around Europe and some adjacent areas.
114 Our goal is to review the current state of knowledge of hydrate occurrence within this area.

115
116 Our study is framed by the offshore stability field for pure methane hydrate in seawater around
117 Europe, estimated from global databases (Fig. 1). The region of stability is most poorly constrained
118 offshore Greenland, where few constraints are available on the geothermal gradient, but is likely to
119 include many of the deeper fjords. The limit of stability lies at varying distances from the coast on the
120 northwest European margin, and hydrate is stable in parts of the Barents Sea and a small part of the
121 Skagerrak. Hydrate is stable in large areas of the western and eastern Mediterranean basins, the
122 Tyrrhenian Sea and the Black Sea, and in small areas of the Adriatic and Aegean Seas and the Sea of
123 Marmara. Hydrate also can be stable beneath permafrost and beneath ice sheets. These settings
124 require more complex hydrate stability calculations that depend on often poorly known parameters.
125 Therefore we have not attempted to carry out such calculations for the whole of our study area.
126 However, in section 4 below we discuss the possibility of hydrate stability beneath permafrost and ice
127 caps onshore Svalbard.

128

129 We first describe the methods that we used to identify areas where the presence of hydrate was
 130 indicated. Then we describe in a series of sections the evidence for hydrate occurrence within these
 131 areas. Finally we synthesise the available evidence on hydrate occurrence in Europe.



132 Figure 1: Pure methane hydrate stability zone around Europe (orange area). Blue marks offshore areas
 133 where pure methane hydrate is not stable, but other forms of hydrate may be stable. The limit of
 134 stability is estimated using the 30 arc-second bathymetry grid from the General Bathymetric Chart of
 135 the Oceans, GEBCO (https://www.gebco.net/data_and_products/gridded_bathymetry_data/), the
 136 0.25° seabed temperature grid from the National Oceanic and Atmospheric Administration, NOAA
 137 (<https://www.nodc.noaa.gov/cgi-bin/OC5/SELECT/woaselect.pl>), a salinity of 3.5% wt, and the
 138 Moridis (2003) phase boundary for Structure I hydrate. Seabed temperature data were interpolated to
 139 match the resolution of the bathymetric grid. Red boxes mark the areas shown in other figures.

141

142 2. Methods

143 To frame our study, we developed a list of hydrate indicators and a workflow for scientific
 144 exploration of marine hydrate; our workflow is adapted from the hydrate petroleum system approach
 145 of Max and Johnson (2014). For a detailed hydrate assessment from an energy resource perspective,
 146 readers are referred to Boswell et al. (2016), and for a complete review on the hydrate systems
 147 concept we refer to Collett et al. (2009).

148

149 2.1 Hydrate indicators

150 We define hydrate indicators as geological, geophysical and geochemical observations that either
151 provide strong evidence to confirm the current presence of hydrate, or simply suggest that hydrate
152 might be present. We considered two categories of hydrate indicators, based on their confidence in
153 confirming the hydrate presence: (i) direct indicators and (ii) indirect indicators. Direct indicators
154 include sampling of hydrate, and observations of hydrate bottom simulating reflectors (BSRs), gas
155 seepage and pore water chlorinity anomalies. Indirect indicators include gas chimneys, anomalies in
156 seismic velocity and electrical resistivity, zones of anomalous reflectivity, the presence of a
157 conventional petroleum province, and various seabed features (cold seeps without gas, backscatter
158 anomalies, mud volcanoes, pockmarks and pingos). Except for the sampling of hydrate, all the other
159 indicators are not only found in hydrate systems and should be considered as hydrate indicators only
160 if they are inferred within or close to the hydrate stability zone (HSZ). In marine settings, the HSZ is
161 the region with appropriate sub-seafloor pressure and temperature conditions to form hydrate. Its
162 thickness is given by the distance between the seabed and the intersection of the thermal structure
163 (obtained using the seabed temperature and geothermal gradient) with a hydrate phase boundary (e.g.,
164 Marín-Moreno et al., 2016).

165
166 A hydrate BSR is a seismic reflector with opposite polarity to the seafloor that generally mimics the
167 seafloor at a depth consistent with the expected base of the HSZ. The presence of a continuous BSR
168 may be an indication of dispersed gas being present in pore water below it rather than being an
169 indicator of the presence of significant hydrate above (e.g., Max and Johnson, 2014). Also, other
170 geological phenomena can create BSRs at different depths (e.g., Berndt et al., 2004). Nevertheless,
171 the presence of a hydrate BSR allows us to constrain the extent of the HSZ (Boswell et al., 2016) and
172 likely requires the presence of at least some hydrate, so we consider it as a direct indicator for hydrate.
173 Hydrate accumulations often have been identified without associated BSRs, for example in the Gulf
174 of Mexico (Majumdar et al., 2016).

175
176 Pore water chlorinity anomalies can arise from dissociation of hydrate during the ascent of a core
177 from the seabed to the surface vessel. Gas seeps from the seabed within the HSZ indicate that pore
178 waters are saturated with gas and therefore hydrate is very likely to be present. Gas escape structures
179 such as pipes and chimneys may be imaged in seismic reflection data and may indicate the presence
180 of hydrate-forming gas within the HSZ. The presence of hydrate increases seismic velocities and
181 electrical resistivities, while the presence of gas decreases seismic velocities but also increases
182 electrical resistivities. High seismic reflectivity (“bright spots”) can result from the presence of
183 subsurface gas, while seismic “blanking”, involving loss of coherent reflectivity, can result from the
184 presence of gas or of chaotic fluid escape structures. Conventional petroleum provinces can provide a
185 source of thermogenic gas entering the HSZ, while the various seabed features listed above provide
186 possible evidence for past or present gas escape through the seabed.

187

188 2.2 Hydrate exploration workflow

189 We developed a hydrate scientific exploration workflow consisting of four clearly defined steps:

- 190 1. Determining the likelihood of hydrate stability.
- 191 2. Imposing better constraints on the likelihood of hydrate presence considering relevant recent
192 geological, physical and chemical changes.
- 193 3. Hydrate petroleum system analysis.
- 194 4. Prospect identification and scientific drilling.

195 The first step is to determine the likelihood of hydrate thermodynamic stability under steady state
196 conditions, i.e., to calculate the HSZ. For this calculation, the bathymetry, seabed temperature, pore
197 water salinity, hydrate forming gases, and geothermal gradient or heat flow need to be known or
198 assumed. In general, sufficient bathymetric data exist or can be easily acquired, but seabed
199 temperature and/or geothermal gradient/heat flow data are generally sparse, and sometimes non-
200 existent. Therefore interpolation/extrapolation techniques need to be employed, with caution to avoid
201 creation of artefacts. In marine environments, the first estimate of the HSZ is commonly made by
202 assuming a salinity of 3.5% and that the hydrate-forming gas is 100% methane.

203

204 The second step involves constraining the likelihood of hydrate presence by assessing existing
205 geological, geophysical and geochemical data. This step also considers the temporal variability of the
206 system and includes: (i) the identification of BSR(s) and their character (continuous or discontinuous)
207 in existing seismic data; (ii) assessment of the sediment thickness that may contain hydrate, based on
208 the identification of source beds and quantification of total organic carbon; (iii) re-assessment of the
209 hydrate-forming gas and its saturation based on possible thermogenic sources; (iv) re-calculation of
210 the HSZ using better constraints on the hydrate-forming gas and any time-dependent parameters
211 affecting the volume of the HSZ, including the influence of geologically recent oceanographic, seabed
212 and tectonic changes on seabed pressure and temperature, geothermal gradient and salinity.

213

214 The third step involves developing a hydrate system analysis, beginning with identifying what
215 additional data need to be acquired. This step might involve the following surveys: (i) a regional 2D
216 seismic survey to study the large scale structure of the geological system and identify BSRs (e.g., Lee
217 et al., 2005); (ii) an ocean bottom seismometer (OBS) survey and/or a 2D long streamer seismic
218 survey to derive information on seismic-wave velocity, porosity, and hydrate and gas saturation (e.g.,
219 Westbrook et al., 2008); (iii) a high resolution local 2D/3D seismic survey to clearly identify direct
220 indicators of hydrate and/or potential clues (e.g., Riedel et al., 2002); (iv) a controlled source
221 electromagnetic survey (CSEM) to impose better constraints in porosity contrasts and pore phase
222 saturations (e.g., Weitemeyer et al., 2006); (v) less well established exploration techniques such as
223 heat flow-based methods for additional information and/or for independent validation of the seismic

224 and electromagnetic observations. Such surveys might lead to a more formal analysis for gas hydrate
225 identification and saturation estimation (e.g., Dai et al., 2008). A joint interpretation approach can be
226 applied to the different geophysical datasets (e.g., Goswami et al., 2015), and focus the interpretation
227 on identifying the depositional environments within and immediately beneath the HSZ, gas sources,
228 and depocentres for sand, turbidite and mass transport deposits, and on assessing the morphology of
229 the sand deposits. At this stage, there are enough data to estimate the approximate volume of methane
230 that might be recoverable from hydrate using average hydrate saturations, and the dominant hydrate
231 distribution and morphology.

232

233 The fourth step, prospect identification, brings the detailed information needed to make an informed
234 decision about scientific drilling targets. This step includes a detailed analysis of seismic and CSEM
235 data to identify features such as sweet spots or structures with enhanced fluid flow, or elevated
236 resistivities or seismic velocities. Such analysis may be followed by rock physics and geotechnical
237 laboratory experiments to determine the elastic (e.g., Priest et al., 2005), electrical (e.g., Spangenberg
238 and Kulenkampff, 2006) and thermo-hydro-mechanical (e.g., Santamarina et al., 2015) properties of
239 hydrate-bearing samples. These properties are then used to calibrate rock physics and geotechnical
240 models (e.g., Marín-Moreno et al., 2017; Uchida et al., 2012) that provide a quantitative
241 understanding of the above properties, of the likely response of the target natural hydrate bearing
242 deposits to natural and/or anthropogenic perturbations, and of local relationships between relevant
243 properties such as porosity and permeability. Then potential drilling targets can be chosen and a
244 geohazard assessment performed for each target to help to decide which, if any, should be prioritized.
245 Finally, scientific drilling should take place to evaluate more fully the prospectivity of the area.

246

247 Below we cover in a series of regional sections the areas where there is evidence for the presence of
248 hydrate. Some large sections of the eastern Atlantic margin have been extensively sampled using both
249 seismic and acoustic techniques, as well as direct sampling. However, to date there are no published
250 reports of hydrate BSRs, gas seeps, chlorinity anomalies or other significant hydrate indicators within
251 or in close proximity to the HSZ. Examples include the northwest margin of the UK and the Bay of
252 Biscay; in both areas, gas seeps have been detected at shelf depths (e.g., Judd et al., 1997; Ruffine et
253 al., 2017) but not in regions of hydrate stability. In most of the areas described below, only the first
254 step and some aspects of the second step have been conducted (Table 1). To date, scientific drilling
255 for hydrate in Europe has been limited to the west Svalbard margin and the western Black Sea, though
256 hydrate has been encountered several times during drilling for other purposes.

257 Table 1: Summary of the most relevant hydrate-related information for all the regions described in the
 258 text. ODP = Ocean Drilling Program; MV = mud volcano; see text for definitions of indicators.

Region	Location	Data	Direct hydrate indicator	Indirect hydrate indicator	Occurrence and host sediment	Gas source and migration path	Hydrate extent and amount
Offshore Greenland	Northeast	ODP 909; 2D seismic; heat flow; seabed temperature	Possible BSR	Gassy sediment sampling; bright spots; chimneys	No hydrate recovered	No information available	Not estimated
	West	Gravity core; 2D & 3D seismic; heat flow; seabed temperature	BSRs	Seismic blanking; oil and gas shows; Ikaite crystals; fluid/gas escape structures; pockmarks	No hydrate recovered	Thermogenic gas; migration through faults and fractures	Not estimated
Offshore Svalbard	Vestnesa Ridge and slope	2D & 3D seismic; OBS; CSEM; cores; MeBo drilling; seafloor imaging; HSZ modelling	Hydrate sampled; gas seeps; BSR	Chimneys; pockmarks; seismic blanking	Topographically & structurally controlled; Small, thin chips, in veins or as chunks in the upper 2-4 m of fine-grained hemipelagic sediments	Dominant thermogenic; thermogenic input increases with depth; thermogenic gas migration through faults	700 km ³ extent of HSZ at ~800-2000 mbsl; saturation from Vp 6-18%; from CSEM 20-30% and 40-68% in chimneys
	Prinz Karl Forland	2D seismic; OBS; CSEM; cores; MeBo drilling; seafloor imaging; HSZ modeling	Hydrate sampled; gas seeps; patchy BSR	Chimneys; bright spots	Hydrate recovered from one pockmark	Microbial with significant thermogenic contribution	Not estimated
	Elsewhere West	2D & 3D seismic; cores; HSZ modelling	Gas seeps; BSRs	Bright spots; gas chimneys	No hydrate recovered	Abiotic gas inferred in the South Molloy Transform Fault & West Knipovich Ridge region	Not estimated
Onshore Svalbard		HSZ modelling; scientific and industry drilling; 2D seismic	None	Hydrate stability; hydrate found offshore; fluid escape structures; gas seeps	Fractured sandstones and shales; coal beds	Partly thermogenic; migration via fractures and seeps	Not estimated
Norwegian Margin	Barents Sea	2D seismic; cores; HSZ modelling	Hydrate sampled; gas seeps; BSRs	Bright spots; chimneys; pockmarks	Structurally controlled; BSRs in consolidated low-porosity sediments and glacial sediments	Mostly thermogenic gas; migration through faults and fractures	Volume 0.19 GSm ³ in Bjornoya Basin; 93-650 GSm ³ in SW Barents Sea or 470-3320 GSm ³ if higher hydrocarbons
	Mid-Norwegian Margin	Core sampling; 2D seismic; OBS; Multi-component seismic; CSEM; HSZ modelling	Hydrate sampled; BSRs	Fluid escape structures; pockmarks	Finely bedded contourite and hemipelagic deposits – mainly silty clays	Microbial with thermogenic component	4000 km ² BSR along N flank of Storegga Slide; saturation 2-10%; volume of 625 GSm ³

259

260 Table 1: Continuation

Region	Location	Data	Direct hydrate indicator	Indirect hydrate indicator	Occurrence and host sediment	Gas source and migration path	Hydrate extent and amount
Offshore Ireland	Rockall and Porcupine Basins	Scientific & industry drilling; 2D & 3D seismic; HSZ modelling	Possible BSRs	Hydrocarbon seeps; fluid escape structures; bright spots	No hydrate recovered	Thermogenic gas migration through faults above active petroleum systems	Not estimated
NW Iberian Margin		Cores; 2D seismic; HSZ modelling	None	Pockmarks; fluid/gas escape structures; seismic blanking; bright spots; chimneys	No hydrate recovered	Not known	Not estimated
Offshore South Iberia & NW Africa Margin	Gulf of Cadiz	Cores; 2D seismic	Hydrate sampled; chlorinity anomalies; BSRs	MV; gas chimneys; pockmarks; degassing structures; seismic blanking; backscatter anomalies	Hydrate found in MV; localised deposits and hosted in fine-grained sediments with low permeability	Thermogenic gas migration through focused fluid flow; abiogenic crustal-derived fluids	Saturation of 5-31% in cores
	Alborán Sea	Cores	Chlorinity anomalies	Gas release from cores	No hydrate recovered	Thermogenic gas from ~5 km depth	Not estimated
	Anaximander Seamount	Cores; HSZ modelling	Hydrate sampled; chlorinity anomalies; gas seeps	MV; pockmarks	Hydrate found in MV	Thermogenic	mm to cm scale disseminated H; saturation of 0.7-16.7%
Eastern Mediterranean	Olimpi Field	Cores	Hydrate sampled; chlorinity anomalies; gas seeps	MV; pockmarks	Hydrate found in MV	Mainly thermogenic	c. 5 GS ^m in Milano dome
	Nile fan and Levant Basin	2D & 3D seismic; seafloor video	Possible BSR; gas seeps	Pockmarks, bright spots, seismic blanking	Sandy buried systems	Mostly microbial; thermogenic at MV	Estimated c. 100 Tcf in the Levant Basin
Sea of Marmara		Cores; 2D & 3D seismic	Hydrate sampled; gas seeps	MV; bright spots; gas chimneys; pockmarks	Thermogenic	Thermogenic G migration from deep Oligocene-Eocene reservoirs	Not estimated

261

262

263

264

265 Table 1: Continuation

Region	Location	Data	Direct hydrate indicator	Indirect hydrate indicator	Occurrence and host sediment	Gas source and migration path	Hydrate extent and amount
Western Black Sea	Bulgaria & Rumania	Cores; 2D & 3D seismic; OBS; CSEM; HSZ modelling	Hydrate sampled; gas seeps; BSRs	Seismic blanking; gas pipes and chimneys; high resistivity values	H formed in levees or base of channels	Microbial	Saturation from CSEM of 30% and from OBS of 10% or 30-40%.
	İğneada	2D seismic, cores	Hydrate sampled; BSRs	Seismic blanking; bright spots; gas chimneys; possible MV	Hydrate fragments in possible MV	Migration via faults and possible MV	Not estimated
	Zonguldak-Amasra	Cores; 2D seismic; HSZ modelling	BSRs	Seismic blanking; MV; gas chimneys	Not known	Thermogenic and microbial	Not estimated
Eastern Black Sea	Samsun	Cores; 2D seismic	None	Seismic blanking; gas chimneys; pockmarks	Not known	Possible hydrogen sulphide in the gas	Not estimated
	Hopa-Rize-Trabzon-Giresun	2D & 3D seismic	BSRs	Seismic blanking; MV; gas chimneys	Not known	Deep thermogenic gas migration through faults and microbial gas	Not estimated

266

267 **3. Offshore Greenland**268 **3.1 Geological Setting**

269 The West Greenland margin formed during Cretaceous to Paleogene continental rifting that
 270 eventually resulted in seafloor spreading in the Baffin Bay and the Labrador Sea (e.g., Oakey and
 271 Chalmers, 2012). A change in spreading direction during the latest Paleocene to Eocene resulted in a
 272 general northward drift of Greenland into the Arctic Ocean, resulting in compression and inversion
 273 that becomes more pronounced the farther north along the Baffin Bay part of the margin. Significant
 274 strike-slope motion along many parts of the margin are also recorded at this time.

275

276 After the cessation of the Caledonian Orogeny during Late Silurian–Early Devonian, the northeast
 277 Greenland margin experienced repeated episodes of rifting with intervening quiescent periods, and
 278 occasionally minor compression and inversion. During the Cretaceous to Paleogene, rifting and
 279 breakup resulted in the onset of opening of the North Atlantic, and continued seafloor spreading
 280 formed large sedimentary basins (Hopper et al., 2014 and references therein). By early Neogene
 281 times, the seafloor spreading resulted in the opening of the Fram Strait and creation of the Atlantic-
 282 Arctic gateway (Jokat et al., 2008; Ritzmann and Jokat, 2003).

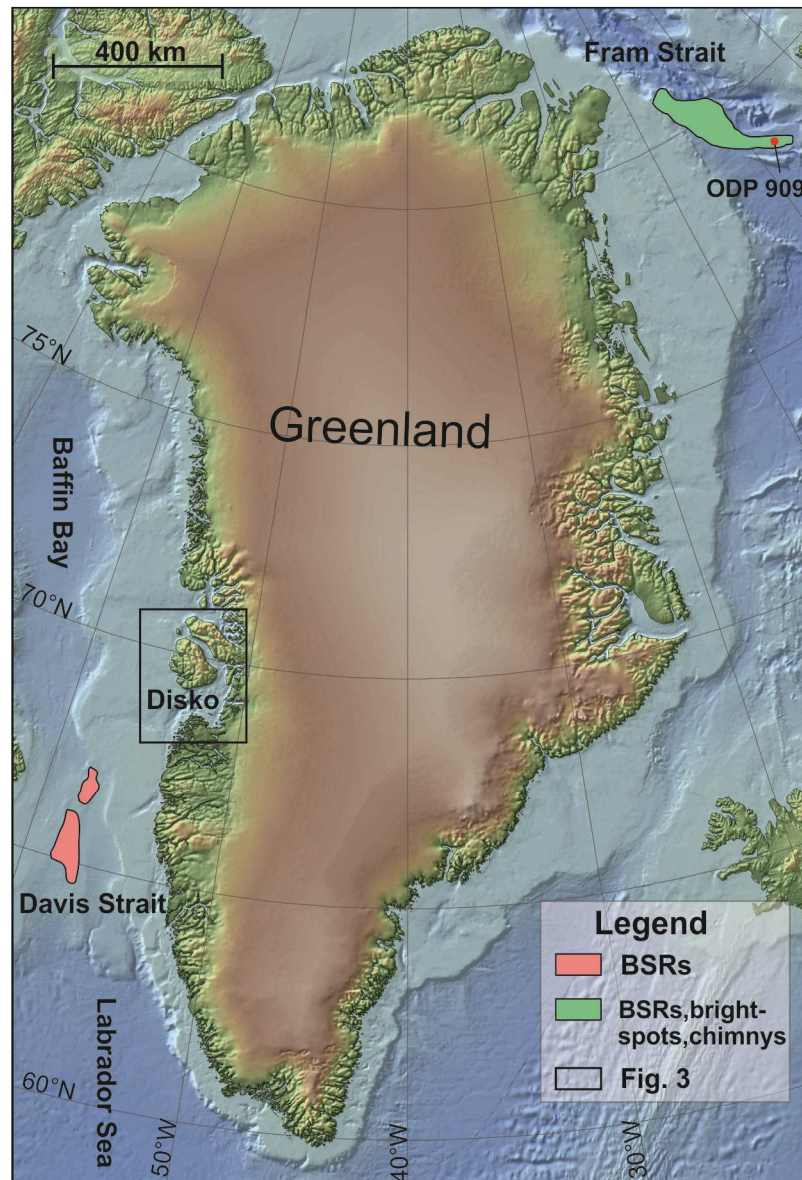
283

284 Along the southeast Greenland margin, no Paleozoic–Jurassic rocks are exposed onshore or otherwise
 285 known to exist. Small outcrops of Cretaceous sediments are known both onshore and offshore (e.g.,

286 Gerlings et al., 2017). Paleocene to Eocene breakup was accompanied by extremely voluminous
 287 volcanism as seafloor spreading was established (e.g., Larsen and Saunders, 1998).

288

289 In late Neogene, all of Greenland's margins became glaciated, resulting in erosion of the inner and
 290 middle shelf areas and deposition of kilometer thick glacial wedges on the outer shelf and slope
 291 areas, while thick contourite deposition occurred in the basinal areas.



292

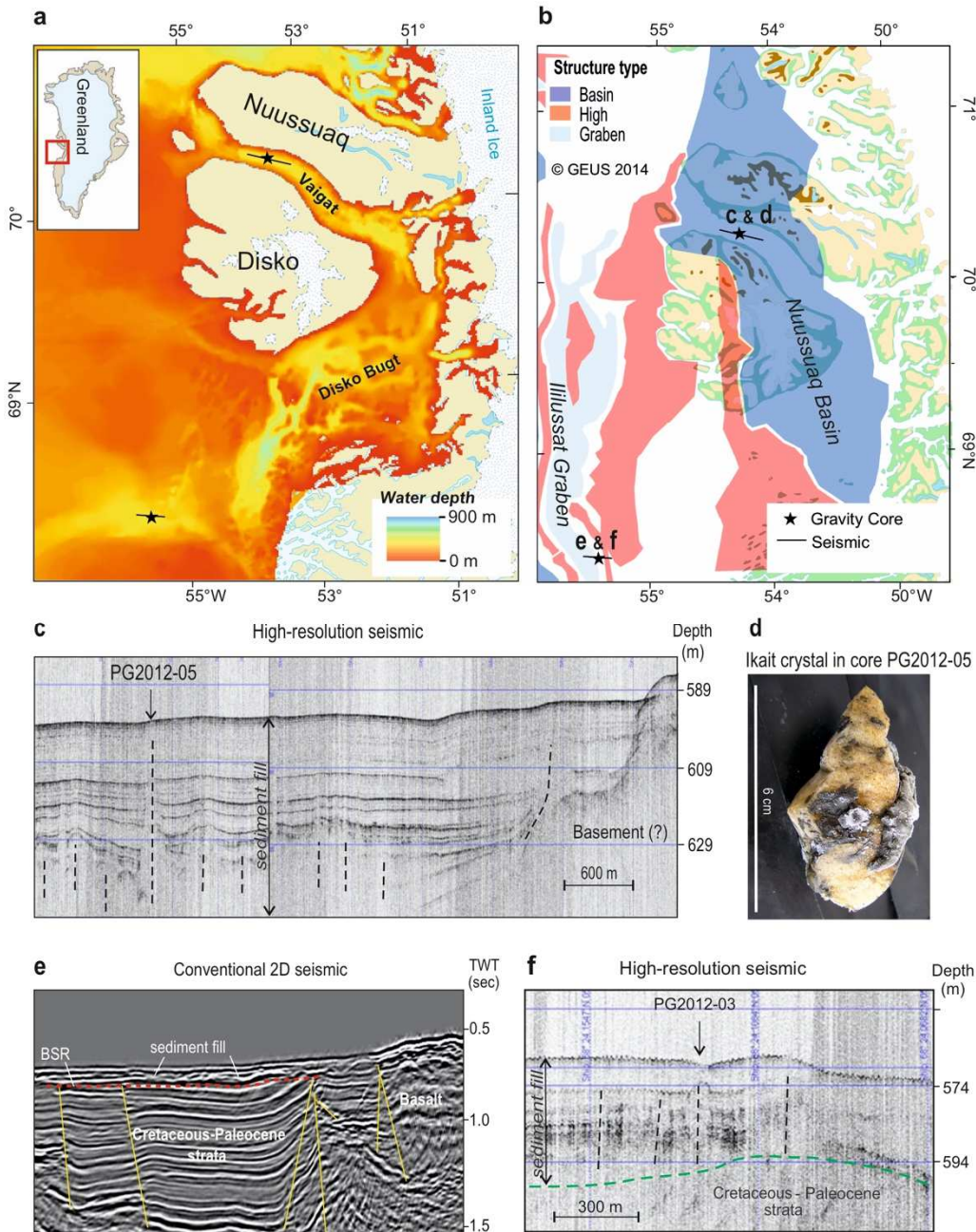
293 Figure 2: Bathymetric map of the Greenland margins and outline of larger offshore areas with seismic
 294 indications of hydrate. Box marks the area shown in Fig. 3.

295

296 3.2 Hydrate occurrence

297 Greenland is surrounded by wide shelf areas with water depths of 200-500 m and 1000-4000 m deep
 298 basinal areas (Fig. 2), all swept by cold bottom water currents. Therefore the Greenland continental
 299 margins should have physical and oceanographic settings suitable for marine hydrate formation. In
 300 addition, a study addressing as yet undiscovered hydrocarbon resources north of the Arctic Circle

301 suggests that the offshore Mesozoic sedimentary basins on the west and northeast Greenland margins
 302 could hold large quantities of oil and gas (Gautier et al., 2011). Due to late Cenozoic uplift and glacial
 303 erosion (Japsen et al., 2006), these basins are now exposed on the shelves at or near the seabed
 304 (Gregersen and Bidstrup, 2008; Hamann et al., 2005; Hopper et al., 2014), increasing the probability
 305 of seepages of gas and thus for formation of hydrate.



306
 307 Figure 3: Indications of hydrate occurrence in the Disko area offshore central west Greenland, where
 308 bottom water temperature is c. 3°C (after Nielsen et al., 2014) a) Bathymetric map with locations of
 309 seismic and cores shown in c)-f) ; b) Simplified map of Cretaceous–Paleogene major structural
 310 elements, outlining the hydrocarbon-bearing Nuussuaq Basin (Bojesen-Koefoed et al., 2007) and the
 311 likely hydrocarbon-bearing Ilulissat Graben (Gregersen and Bidstrup, 2008), with locations of seismic
 312 and cores; c) High-resolution seismic line along Vaigat showing younger sediments with chimneys
 313 (dashed black lines) indicating gas/fluid seepage from below, and location of gravity core PG2012-05
 314 taken on top of one of these features; d) 6-cm-long ikait crystal collected from the core catcher of

315 gravity core PG2012-05, presumably originating from seepage of methane; e) 2D seismic record
316 showing a seabed depression with sub-cropping faulted Cretaceous–Paleocene strata (yellow lines)
317 and a BSR at about 75 ms sub-bottom depth (red dashed line); f) High-resolution seismic line inside
318 the seabed depression, showing Cretaceous–Paleocene strata overlain by younger sediments that are
319 disrupted by gas/fluid escape features (black dashed lines). Gas-bearing gravity core PG2012-03 was
320 located in a pockmark underlain by a large diapiric feature.
321

322 Nevertheless, little work has been done on the hydrate potential of offshore Greenland. At present,
323 most of the available data derive from conventional oil and gas exploration, including more than
324 100,000 km of 2D seismic reflection data offshore west and northeast Greenland as well as several 3D
325 surveys on the western margin. Some information of heat flow and seabed temperature data offshore
326 Greenland exist, but these are sparse and mostly limited to the few exploration wells that have been
327 drilled along the western margin. Echo-sounder, high-resolution subbottom profiler and swath
328 bathymetry data exist for smaller areas along all the margins, but most are not in the public domain.
329

330 Offshore northeast Greenland no commercial wells have been drilled yet. However, in the southern
331 Fram Strait, Ocean Drilling Program (ODP) well 909 encountered gassy sediments (Knies and Mann,
332 2002), which can be traced up-slope the northeast Greenland margin, where bright spots, chimneys
333 and possible BSRs indicate that hydrate may be present (Fig. 2; Nielsen and Jokat, 2009). Offshore
334 west Greenland, several commercial wells have gas and oil shows, but there have been no significant
335 discoveries so far. Several oil seeps as well as hydrate and gas encountered by shallow onshore
336 drilling demonstrate that working petroleum systems exist in the Nuussuaq Basin (Fig. 3; Bojesen-
337 Koefoed et al., 2007; Christiansen et al., 1994; Pedersen et al., 2006). A pilot study of the marine part
338 of the Nuussuaq Basin found various indirect indicators for the presence of hydrate in shallow seismic
339 and gravity core data (Nielsen et al., 2014; Fig. 3), demonstrating that the offshore part of the
340 Nuussuaq Basin likely contains significant quantities of hydrate. Further offshore west Greenland, in
341 the up to 700 m deep Davis Strait area (Fig. 2), BSRs with associated amplitude variations indicating
342 hydrate above free gas can be seen on several seismic profiles (Nielsen et al., 2000), further
343 demonstrating a possible marine hydrate occurrence in the region.
344

345 Direct sampling of hydrate offshore Greenland has not been reported to date and, despite the above-
346 mentioned indications of hydrate presence, no systematic study or compilation has yet been
347 undertaken. In addition, due to the very sparse information on heat flow and seabed temperature, there
348 is currently no published detailed study of the hydrate stability zone offshore Greenland.
349

350 **4. Offshore and onshore Svalbard**

351 4.1 Geological Setting

352 The west Svalbard margin shares a common geological history with the northeast Greenland margin
353 (section 3.1) until the opening of the Fram Strait. Subsequently, deep-water circulation between the

354 Arctic Ocean and the Norwegian-Greenland Sea led to deposition of thick contourite sequences that
355 extend from the Svalbard margin towards the mid-ocean ridges. Two sediment types dominate the
356 west Svalbard margin: glaciogenic debris flows in trough mouth fans beyond the shelf break; and
357 turbiditic, glaciomarine and hemipelagic sediments, which are to some extent reworked by contour
358 currents (Vorren and Laberg, 1997; Vorren et al., 1998). The eastern margins of the Fram Strait were
359 dominated by contourites during the late Miocene to Pleistocene (Mattingsdal et al., 2014) leading to
360 the development of large sediment drifts such as the Vestnesa Ridge (Fohrmann et al., 2001) on
361 young and relatively warm oceanic crust. The Vestnesa Ridge is located in the eastern Fram Strait at
362 $\sim 79^\circ\text{N}$, north of the Knipovich Ridge and Molloy transform fault (Fig. 4), representing one of the
363 northernmost occurrences of hydrate in the world.

364

365 In contrast, the Svalbard archipelago is the most uplifted part of the Barents Shelf and is dominated by
366 older strata providing a “window” into the tectono-stratigraphic evolution of the Barents Sea area.
367 Approximately 60% of the archipelago is covered by glaciers, with the remainder strongly affected by
368 continuous permafrost. Ice caps are found predominantly in northeastern Svalbard, with ice
369 thicknesses of up to 550 m observed for the Austfonna ice cap on Nordaustlandet (Furst et al., 2018).
370 Permafrost thickness varies from less than 100 m in coastal settings to over 500 m in the highlands
371 (Humlum et al., 2003). The nearly complete Devonian-Paleogene stratigraphic record is exceptionally
372 well exposed due to the lack of vegetation, giving insights into reservoir and source rock intervals
373 targeted further south (Henriksen et al., 2011b; Nøttvedt et al., 1993; Worsley, 2008).

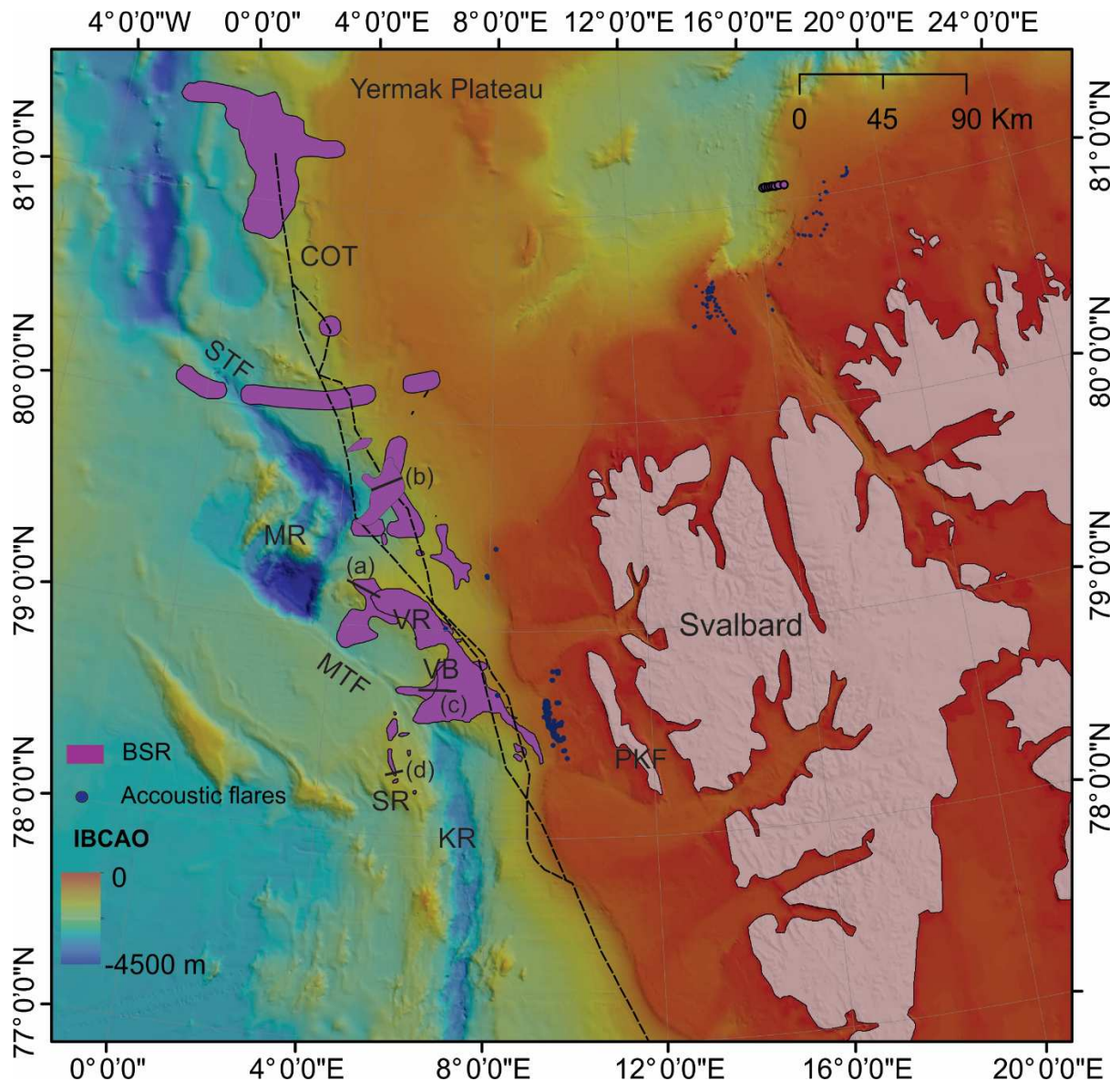
374

375 4.2 Hydrate occurrence

376 4.2.1 Offshore west Svalbard

377 The presence of a prominent hydrate BSR was revealed by several seismic reflection studies in the
378 Vestnesa basin (e.g., Dumke et al., 2016; Eiken and Hinz, 1993; Vanneste et al., 2005; Fig. 4). The
379 BSR can be traced from the continental slope at c. 800 m water depth to the Molloy Transform Fault
380 and beyond to > 2000 m water depth (Hustoft et al., 2010; Sarkar et al., 2012; Vanneste et al., 2005).
381 It appears as a nearly continuous reflection with amplitudes that vary laterally and generally decrease
382 towards the flanks of sedimentary ridges (Fig. 5). This variation indicates that hydrate and gas
383 accumulations are primarily topographically and structurally controlled (Bünz et al., 2012). The BSR
384 covers the whole of the Vestnesa Ridge (i.e., from c. 1100 m to 1700 m water depth), exhibiting a
385 strong impedance contrast between hydrate-bearing and gas-charged sediments (Bünz et al., 2012;
386 Petersen et al., 2010; Plaza-Faverola et al., 2017). An interconnected zone of free gas beneath the
387 BSR is more prominent along the eastern segment of the Vestnesa Ridge, where currently active gas
388 seepage is concentrated (Hustoft et al., 2009; Panieri et al., 2017; Smith et al., 2014). Faults are
389 identified on seismic profiles, extending from the seafloor to beneath the BSR. These faults control
390 the ascent of fluids and the distribution of gas seeps on the Vestnesa Ridge (Plaza-Faverola et al.,

391 2015; Vanneste et al., 2005). Basin modeling studies show that generation of thermogenic gas from
 392 relatively shallow and young source rocks sustains shallow gas and hydrate accumulations, at least
 393 within the eastern part of the Vestnesa basin (Dumke et al., 2016; Knies et al., 2014). In this setting,
 394 very close to the mid-ocean ridge, the hydrate system is strongly influenced by the young and hot
 395 oceanic crust. Geothermal gradients increase gradually from 70 to 115 °C/km towards the Molloy
 396 Transform Fault (Crane et al., 1991; Vanneste et al., 2005).
 397

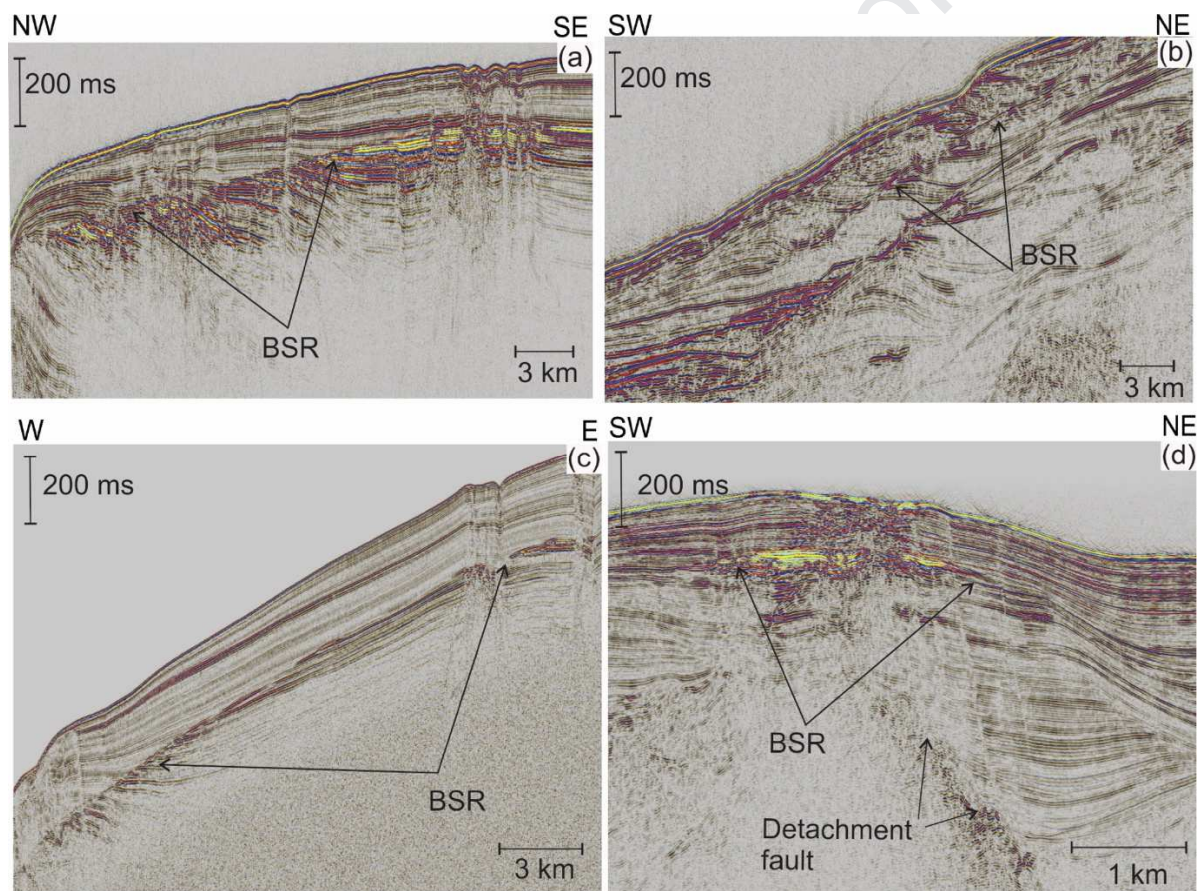


398 Figure 4: BSR distribution projected over IBCAO bathymetry off Svalbard. The BSR outline
 399 corresponds to observations from Vanneste et al. (2005); Petersen et al. (2010); Hustoft et al. (2009);
 400 Sarkar et al. (2012); Bünz et al. (2012); Geissler et al. (2014); Johnson et al. (2015); (Dumke et al.,
 401 2016); Plaza-Faverola et al. (2017); and Waghorn et al. (2018). Gas flares compiled from multiple
 402 expeditions to the area by NOC, AWI, CAGE. PKF=Prins Karl Forland; COT=Continent-Ocean
 403 Transition (Engen et al., 2008); KR=Knipovich Ridge; MR=Molloy Ridge; VR=Vestnesa Ridge;
 404 VB=Vestnesa Basin; SR=Svyatogor Ridge; MTF=Molloy Transform Fault; STF=Spitsbergen
 405 Transform Fault. (a)-(d) mark seismic profiles shown in Fig. 5.
 406
 407

408 South of the Molloy Transform Fault and to the west of the Knipovich ridge spreading axis, a well-
 409 developed hydrate system has been documented along the Svyatogor ridge, a contourite drift similar
 410 to the Vestnesa Ridge (Fig. 4, 5). Here the gas hydrate system is believed to be sustained by input of
 411 abiotic gas, a product of serpentinization at detachment faults (Johnson et al., 2015; Waghorn et al.,
 412 2018).

413

414 Elsewhere on the west Svalbard Margin, the BSR is weak and in some areas it is patchy (e.g., Geissler
 415 et al., 2014). Observations of shallow gas in accumulations that roughly follow the seafloor further
 416 upslope on the continental margin may be linked to hydrate dissociation (Riedel et al., 2018; Sarkar et
 417 al., 2012). To the west and east of the Yermak Plateau, relatively weak BSRs and some double BSRs
 418 have been documented (e.g., Geissler et al., 2014).



419

420 Figure 5: Examples of BSRs offshore west-Svalbard: (a) western segment of the Vestnesa Ridge
 421 (Plaza-Faverola et al., 2017); (b) western flank of Yermak Plateau (Geissler et al., 2014); (c) slope
 422 between Prins Karl Forland and the Molloy Transform Fault (Vanneste et al., 2005); (d) southern part
 423 of the Svyatogor Ridge (Johnson et al., 2015; Waghorn et al., 2018). The location of each example is
 424 indicated in Fig. 4. The BSR is continuous and strong along the Svyatogor Ridge, the Vestnesa Ridge
 425 and its southern flank. The BSR is weak and patchy towards the Yermak Plateau.

426

427 Hydrate has been recovered from several of the pockmarks that lie above chimney structures on the
 428 eastern Vestnesa Ridge segment. Here, hydrate appears as small, thin chips, in veins or as chunks of
 429 several 10s of cm, embedded in the upper 2-4 m of muddy sediments (e.g., Panieri et al., 2017; Smith

430 et al., 2014). The gas compositions of these hydrate samples and of core head-space gas samples
431 provide strong evidence for a thermogenic input into the HSZ (Plaza-Faverola et al., 2017; Smith et
432 al., 2014). Massive hydrate has been collected in a zone of weak BSRs at a focused fluid flow
433 structure on the continental slope (e.g., Graves et al., 2017; Sarkar et al., 2012). Hydrate is suspected
434 but so far not found in regions where the HSZ pinches out near the shelf break off Prins Karl Forland,
435 where pervasive seepage exists (e.g., Berndt et al., 2014; Wallmann et al., 2018; Westbrook et al.,
436 2009). A HSZ volume of ca. 700 km³ was derived from mapped BSRs in the Vestnesa Basin (Plaza-
437 Faverola et al., 2015).

438

439 Several studies provide constraints on hydrate saturations on the eastern Vestnesa Ridge based on P-
440 wave velocity variations from seismic data and resistivity from CSEM data. From P wave velocity
441 anomalies, Hustoft et al. (2009) estimated mean hydrate saturations of ~6% within a 30-100 m thick
442 zone above the BSR, reaching a maximum of 11%. Their velocity model was derived from multi-
443 channel seismic reflection data along an E-W profile that intersects the crest of the Vestnesa ridge at
444 the eastern end of an area of active seepage. They found the highest hydrate saturations at the crest of
445 the ridge and near fault zones. In a more recent study along the ridge crest nearby, Singroha et al.
446 (2019) estimated hydrate saturations of 10-18% of the pore space within a 100 m thick zone above the
447 BSR, based on P wave velocities and full waveform inversion of wide-angle seismic data from OBSs.
448 By comparison, joint analysis of resistivity from CSEM data and OBS data along a transect in the
449 same area suggests mean hydrate saturations of 20-30% outside of chimney structures and 40-68% in
450 the lowermost c. 80 m of the HSZ within a highly brecciated gas chimney (Goswami et al., 2015).
451 Despite similar velocities to those of Hustoft et al. (2009) and Singroha et al. (2019), these estimated
452 saturations are much higher because free gas is assumed to co-exist with hydrate in the HSZ,
453 contributing positively to the resistivity anomaly and negatively to the velocity anomaly. All three
454 studies systematically found the highest hydrate saturations associated with faults and fractures within
455 the GHZ. The free gas saturations estimated by these studies in zones outside gas chimneys
456 consistently range between 1.5 and 4% of the pore space within a low-velocity zone below the BSR.

457

458 4.2.2 Onshore Svalbard

459 As part of early petroleum exploration of the Barents Sea, eighteen petroleum exploration wells were
460 drilled on Svalbard from 1961 to 1994 (Senger et al., 2017). While none of these wells resulted in
461 commercial discoveries, numerous boreholes encountered gas. In addition, research drilling in
462 Adventdalen and coal exploration in Petuniabukta discovered producible natural gas, some of which
463 is directly associated with permafrost (Senger et al., 2019). These discoveries, as well as the presence
464 of hydrate offshore (Section 4.2.1), prompted efforts to assess the feasibility of finding hydrate
465 onshore Svalbard (Betlem et al., 2019).

466

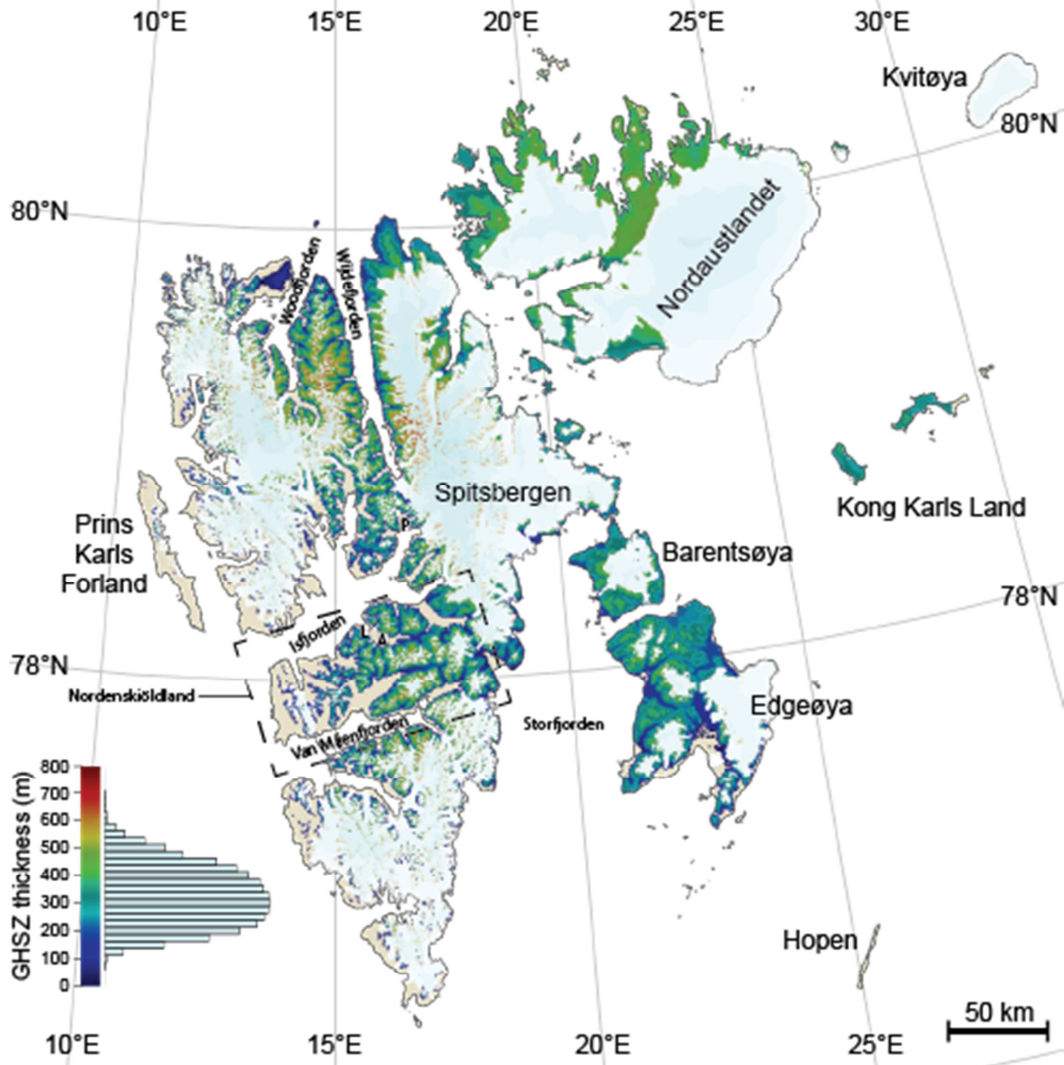
467 Recent modelling efforts constrain a potentially stable marine hydrate stability zone in the fjords
468 around Svalbard (Betlem, 2018; Roy et al., 2012), and a permafrost-associated hydrate stability zone
469 onshore central Spitsbergen (Betlem et al., 2019). The latter has been extended to all unglaciated areas
470 of Svalbard's main islands (Spitsbergen, Nordaustlandet, Prins Karls Forland, Barentsøya and
471 Edgeøya; Fig. 6). Thus far hydrate has not been directly sampled onshore Svalbard, largely due to a
472 lack of dedicated exploration efforts. Circumstantial evidence for probable hydrate presence is
473 provided by long-term gas bubbling in numerous coal exploration boreholes (Jochmann, M., pers.
474 comm. 2017), though these are unfortunately not well documented.

475
476 Thus the Svalbard archipelago possesses three important factors contributing to the presence of
477 hydrate: 1) suitable thermobaric conditions, 2) an active petroleum system, and 3) a constant flux of
478 thermogenic and microbial gas. Suitable thermobaric conditions (i.e., shallow-to-deep permafrost) are
479 brought about by laterally changing mean annual air temperatures of between $-3.5\text{ }^{\circ}\text{C}$ and $-8\text{ }^{\circ}\text{C}$
480 (Betlem et al., 2019; Przybylak et al., 2014). Where permafrost surpasses 100-125 m depth,
481 subsurface thermal regimes are cold enough to allow hydrate formation under hydrostatic pressure.
482 Thickening of ice caps and glaciers towards the north is likely to contribute further to local regions of
483 hydrate stability as a result of loading (i.e., pressure increase) and favourable thermal regimes at
484 glacier bases. However, the extent of hydrate stability remains difficult to assess due to uncertainties
485 in properties such as sub-glacial thermal state, densities, and local thicknesses, as well as the limited
486 resolution and accuracy of relevant datasets.

487
488 Widespread organic-rich source rocks (e.g., Upper Jurassic to Lower Cretaceous Agardhfjellet
489 Formation and Middle-Triassic Botneheia Formation) and coal beds (e.g., Lower Carboniferous
490 Billefjorden Group and Paleogene Firkanten Formation) may act as unconventional reservoirs hosting
491 disseminated or fracture-filled hydrate. These Mesozoic organic rich source rocks have the same
492 origin as those contributing to hydrocarbon discoveries in the Barents Sea (Abay et al., 2014) and
493 have been linked to hydrocarbon finds onshore. Suitable reservoir rocks are found in both sandstone-
494 dominated sequences (e.g., the Paleogene Van Mijenfjorden Group, the Lower Cretaceous
495 Helvetiafjellet Formation and the Upper Triassic-Middle Jurassic Wilhelmøya Subgroup) and
496 carbonates (e.g., the Permian Tempelfjorden and Gipsdalen Groups). Limited reservoir quality, with
497 poor matrix porosity and permeability related to extensive diagenesis (e.g., Mork, 2013) is a major
498 challenge. However, pervasive natural fracturing contributes by enhancing fracture-related fluid flow
499 (Ogata et al., 2012).

500
501 Significant quantities of thermogenic gas (mixed with microbial gas in shallower intervals) were
502 encountered during research drilling for the Longyearbyen CO₂ Lab project in Adventdalen (Ohm et
503 al., 2019) and in petroleum and coal exploration wells (Senger et al., 2019). Furthermore, high

504 concentrations of microbial gas are observed in onshore pingo discharge waters (Hodson et al., 2019).
 505 Gas flares, pockmarks and thermogenic methane are observed in several fjords of Svalbard (Liira et
 506 al., 2019; Roy et al., 2019). Thus there is evidence for active fluid seepage both onshore and offshore.
 507



508
 509 Figure 6: Thickness of the HSZ onshore Svalbard, for a plausible gas composition of 93% methane,
 510 7% ethane and seawater salinity. Geothermal gradients are derived from boreholes and inferred from
 511 the depth of the base of permafrost thickness in central Spitsbergen (Betlem, 2018; Betlem et al.,
 512 2019). Lapse rate is set at $-6\text{ }^{\circ}\text{C}/\text{km}$, and surface air temperatures are incorporated from Przybylak et
 513 al. (2014). A: Adventdalen; L: Longyearbyen; P: Petuniabukta. The map uses topographic and
 514 coastline data from the Norwegian Polar Institute.
 515

516 Assuming that structure I hydrate dominates, a zone of hydrate stability likely occurs in the interior of
 517 Spitsbergen along a relatively unglaciated corridor stretching from Nordenskiöldland in the centre to
 518 Wijdefjorden in the north. Strandflats and valley systems limit hydrate stability on Svalbard's western
 519 flanks due to elevated temperatures associated with the West Spitsbergen Current (Przybylak et al.,
 520 2014). Mean annual temperatures decrease to the east, so that similar settings on Edgeøya, Barentsøya
 521 and Nordaustlandet fall well within the hydrate stability field, even in coastal settings. Most of the

522 archipelago thus appears to be on the edge of hydrate stability, with vertical and lateral variations
523 tipping particular locations in and out of the hydrate stability field.

524

525 **5. Norwegian Margin**

526 5.1 Geological setting

527 The Barents Sea is a large epi-continental shelf sea bound by the North Atlantic to the west, the
528 Norwegian and Russian landmasses to the south, the Arctic Ocean to the north and Novaya Zemlya to
529 the east. Formed in association with the opening of Norwegian-Greenland Sea and Eurasia Basin
530 during the Cenozoic (Faleide et al., 1984), it is composed of a complex mosaic of basins, platforms,
531 and structural highs and is a major petroleum province (Doré, 1995; Nøttvedt et al., 1988). Tectonic
532 uplift, erosion and multiple glaciations affected the Barents Sea during the Cenozoic and resulted in
533 the removal of up to 2 km of sediments from the region (Henriksen et al., 2011a; Ktenas et al., 2017;
534 Vorren et al., 1991). These processes resulted in the spillage of hydrocarbons from reservoir rocks,
535 and recent exploration has shown predominantly gas reservoirs and underfilled reservoirs with low oil
536 saturation (Doré and Jensen, 1996; Henriksen et al., 2011a).

537

538 Along the mid-Norwegian margin, the Møre and the Vøring basins are the two most prominent. They
539 developed as a result of several rifting episodes until Late Paleocene/Early Eocene continental break-
540 up (Brekke, 2000; Lundin and Doré, 1997). Post break-up thermal subsidence during the Cretaceous
541 resulted in up to 10-km-thick sedimentary basin fill. The second youngest sedimentary succession is
542 the Miocene/lowermost Pliocene Kai Formation with predominantly fine-grained hemipelagic
543 sediments (Dalland, 1988; Rise et al., 2005). The overlying Naust formation encompasses sediments
544 of the Plio-Pleistocene glacial-interglacial cycles that significantly changed the sedimentation pattern,
545 yielding a thick wedge of clastic sediments on the shelf (Hjelstuen et al., 1999; Stuevold and Eldholm,
546 1996). Within this formation, contourites deposited along slope during deglaciation and interglacials
547 frequently interlayer the glaciogenic downslope-transported debris flows (Laberg et al., 2001). A mass-
548 wasting event, the Storegga Slide, removed large amounts of sediment within the Møre Basin and
549 along its northern border with the Vøring Plateau at about 8.2 ka (Bryn et al., 2005).

550

551 5.2 Hydrate occurrence

552 5.2.1 Barents Sea

553 Leaking reservoirs in the Barents Sea have given rise to widespread occurrence of fluid-flow features
554 such as shallow gas accumulations, gas seeps, gas chimneys, pockmarks of various sizes, pingos and
555 hydrate (Fig. 7; Andreassen et al., 2017; Chand et al., 2012; Laberg and Andreassen, 1996; Rise et al.,
556 2015; Serov et al., 2017; Vadakkepuliyaambatta et al., 2013; Vadakkepuliyaambatta et al., 2017). Fluid
557 migration in the area is structurally controlled, with major faults and fractures acting as pathways
558 (Vadakkepuliyaambatta et al., 2013).

559

560 The presence of hydrate has been inferred at multiple locations in the Barents Sea from BSRs in
561 multi-channel seismic data (Vadakkepuliyaambatta et al., 2017 and references therein). BSRs occur in
562 close association with vertical fluid-flow systems, shallow gas accumulations, faults, and fractures
563 (Ostanin et al., 2013; Vadakkepuliyaambatta et al., 2013; Vadakkepuliyaambatta et al., 2017;
564 Vadakkepuliyaambatta et al., 2015). They generally occur in consolidated sediments of Jurassic and
565 younger ages as well as in the glacial sediments of Pleistocene to Holocene age (e.g., Andreassen et
566 al., 1990; Vadakkepuliyaambatta et al., 2017). Although multiple active seeps have been detected in
567 the southwest Barents Sea (e.g., Andreassen et al., 2017; Chand et al., 2012), no hydrate sample has
568 been recovered yet. However, in the Storfjordrenna region of the northwest Barents Sea, Serov et al.
569 (2017) reported sampling of hydrate just below the seafloor. Hydrate was also recovered on the
570 continental slope of southwest Barents Sea at the Håkon Mosby mud volcano (Ginsburg et al., 1999).

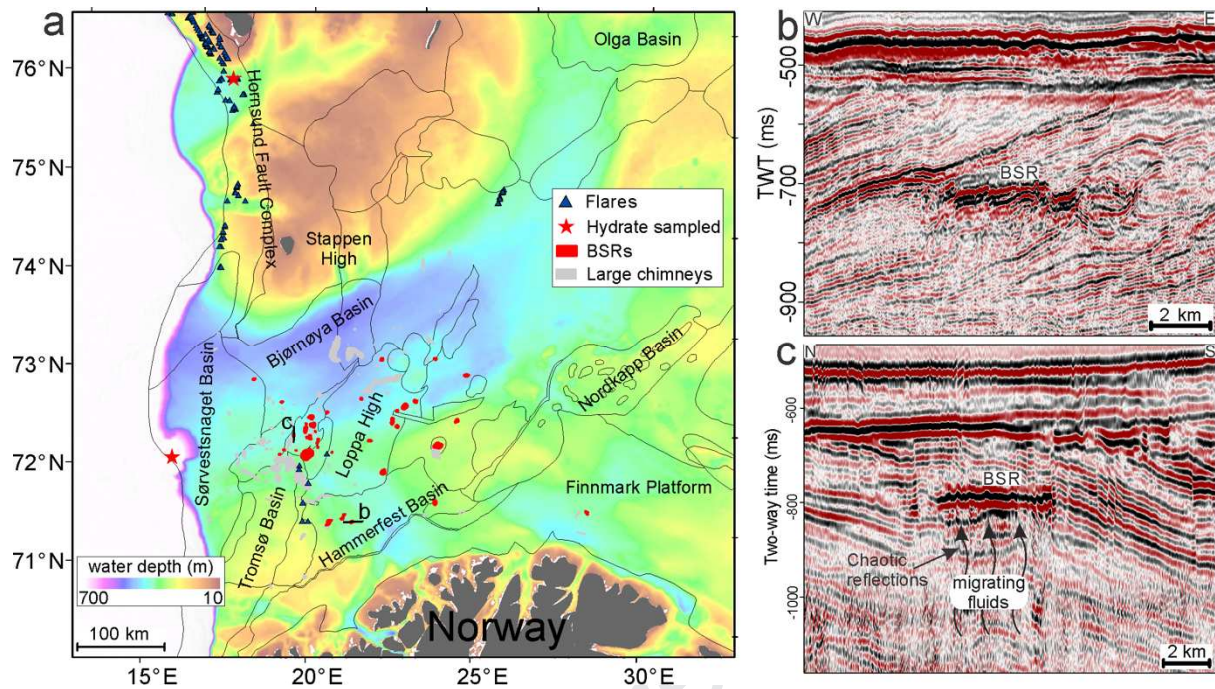
571

572 Results from thermal modelling suggest a prevalence of thermogenic methane and higher order
573 hydrocarbons forming hydrate in the region (Chand et al., 2008; Vadakkepuliyaambatta et al., 2017).
574 Methane hydrate is not stable in most parts of the Barents Sea, primarily due to the shallow water
575 depth (<350 m; Chand et al., 2008; Klitzke et al., 2016; Vadakkepuliyaambatta et al., 2017). Hydrate
576 occurrence is highly variable, controlled primarily by thermogenic gas discharge into the shallow
577 sediments (Vadakkepuliyaambatta et al., 2017). Variations in the geothermal gradient, salt tectonics,
578 and the inflow of warm Atlantic water also influence hydrate stability in the region (Chand et al.,
579 2008; Vadakkepuliyaambatta et al., 2017). Major factors controlling hydrate stability, such as the
580 bottom water temperature and geothermal gradient, vary greatly across the various basins and highs of
581 southwest Barents Sea. Bottom-water temperatures can vary between 1 and 6 °C across the region,
582 where warm Atlantic waters mix with cold Arctic waters (Vadakkepuliyaambatta et al., 2017).
583 Seasonal variations in bottom water temperature are up to 2 ° C (Ferré et al., 2012). Geothermal
584 gradients vary from 25 to 65 ° C/km, mainly due to the presence of salt diapirs on the eastern part of
585 this area (Bugge et al., 2002). The southwest Barents Sea may be a focus of hydrate dissociation due
586 to ocean warming in the near future (Vadakkepuliyaambatta et al., 2017).

587

588 The volume of hydrate in the Barents Sea is still uncertain, primarily due to the uncertainties related
589 to gas composition, hydrate saturation and hydrate distribution within the host sediments. Based on
590 multi-channel seismic data and well logs, Laberg et al. (1998) estimated ~0.19 GSm³ (GSm³ = 10⁹
591 standard cubic metres) of gas hydrate trapped within the Eocene succession of a small part of
592 Bjørnøya Basin where a BSR was observed. Vadakkepuliyaambatta et al. (2017) proposed a hydrate
593 volume of ~93-650 GSm³ in the southwest Barents Sea from hydrate stability models that assumed
594 that the hydrate-forming gas was pure methane. Due to the presence of higher-order hydrocarbons, the
595 hydrate volume could be as high as ~470–3320 GSm³. The patchy occurrence of hydrate systems in

596 the southwest Barents Sea and their occurrence in consolidated, low-porosity sediments indicates low
 597 resource density for economic exploitation.



598
 599 Figure 7: a) Bathymetry of the western Barents Sea with locations of hydrate indicators (compiled
 600 from Andreassen et al., 2017; Chand et al., 2012; Mau et al., 2017; Serov et al., 2017;
 601 Vadakkepuliambatta et al., 2013; Vadakkepuliambatta et al., 2017). b) and c) Seismic examples of
 602 a BSR in the southwest Barents Sea clearly cross-cutting the tilted sedimentary strata and showing
 603 reversed polarity compared to the seafloor reflection (modified from Vadakkepuliambatta et al.,
 604 2017).

605

606 5.2.2 Mid-Norwegian margin

607 Bugge et al. (1988) first recognised evidence for hydrate in the northern Storegga Slide area of the
 608 mid-Norwegian Margin in the form of a weak BSR. Later, Posewang and Mienert (1999) and Bouriak
 609 et al. (2000) confirmed the geophysical evidence that hydrate exists in this area. In high-resolution
 610 seismic data, the BSR is generally characterised as an abrupt upper boundary of increased reflection
 611 amplitude (Fig. 8a; Bouriak et al., 2000; Bünz et al., 2003). In areas of dipping seafloor the BSR is
 612 readily identified cross-cutting the almost horizontally layered strata.

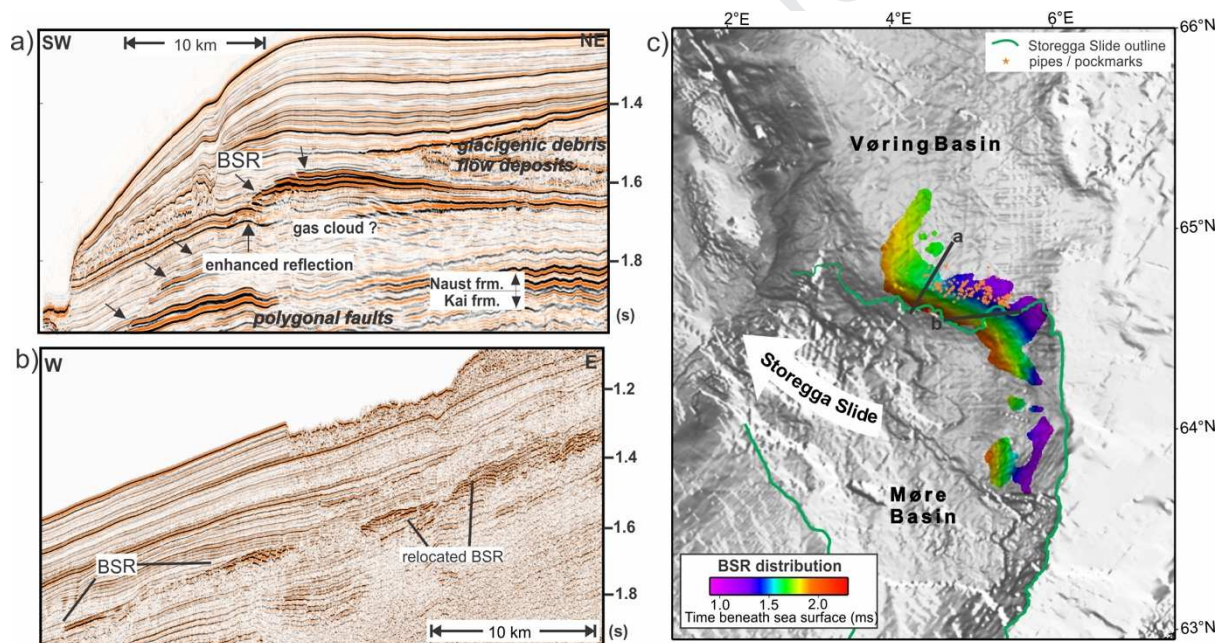
613

614 A double BSR observed in a small area along the northern flank of the Storegga Slide is attributed to
 615 a hydrate structure involving high-order hydrocarbons (Andreassen et al., 2000; Posewang and
 616 Mienert, 1999). Analysis of multi-component seismic data does not show a BSR in shear-wave
 617 components, indicating that hydrate here does not increase the shear stiffness of the sediments
 618 (Andreassen et al., 2003; Bünz et al., 2005). The presence of a BSR inside the slide area indicates that
 619 the hydrate system is dynamically adjusting to post-slide pressure-temperature equilibrium conditions
 620 (Fig. 8b; Bouriak et al., 2000; Bünz et al., 2003).

621

622 Bünz et al. (2003) mapped the extent of the BSR, which predominantly occurs over an area of about
 623 4000 km² on the mid-Norwegian margin along the northern flank of the Storegga Slide (Fig. 8c). The
 624 glacial evolution of this margin resulted in widespread deposition of glacial sediments that built out
 625 the continental shelf (e.g., Hjelstuen et al., 2005; Stuevold and Eldholm, 1996). These low-
 626 permeability sediments are not conducive to hydrate growth and limit the extent of hydrate to the
 627 northern flank of the Storegga Slide, where they occur in marine contourite deposits. The large-scale
 628 distribution of hydrate in this area can be classified as a stratigraphic accumulation. The hydrate
 629 occurrence coincides with a vertical fluid flow system as documented by features such as pockmarks
 630 on the seafloor and pipe and chimney structures in subsurface seismic data (Bouriak et al., 2000; Bünz
 631 et al., 2003; Hustoft et al., 2010; Hustoft et al., 2007). A hydrate stability model was developed by
 632 Mienert et al. (2005), who speculated that ocean warming since the last deglaciation promoted the
 633 development of instabilities along the mid-Norwegian margin.

634



635

636 Figure 8: Examples of BSRs on the mid-Norwegian margin (modified from Bünz and Mienert, 2004):
 637 a) typical expression of a BSR identified as an abrupt upper boundary of increased reflection
 638 amplitude, occurring in glaciomarine contourite deposits along the northern flank of the Storegga
 639 Slide (vertical exaggeration ~35). b) The BSR also occurs inside the Storegga Slide area where it has
 640 readjusted to post-slide pressure-temperature equilibrium conditions (vertical exaggeration ~33). c)
 641 The BSR predominantly occurs along the northern Storegga Slide flank and patchily west of the
 642 Storegga Slide headwall over a total area of 4000 km².

643

644 Velocity analyses of seismic data provided evidence for the existence of hydrate in sub-seafloor
 645 sediments (Bünz and Mienert, 2004; Bünz et al., 2005; Plaza-Faverola et al., 2010; Westbrook et al.,
 646 2008). Hydrate saturations have been estimated from OBS data and range from 2 to 15% of pore
 647 space. The first hydrate sample in this area was from a pockmark in the Nyegga area, located at the
 648 northeastern corner of the Storegga Slide (Ivanov et al., 2007). Isotopic analysis of the gas in hydrate

649 from this pockmark suggests a primarily microbial origin but with a significant thermogenic
650 component (Vaular et al., 2010). In the Nyegga area, many focused fluid flow structures pierce the
651 HSZ (Hjelstuen et al., 2010; Hustoft et al., 2010; Plaza-Faverola et al., 2011) and form such
652 pockmarks at the seafloor (Hovland et al., 2005; Mazzini et al., 2006). Analysis of velocities from
653 wide-angle seismic data and resistivities from CSEM data showed that these chimneys likely contain
654 much larger amounts of gas hydrate than the surrounding stratified sediments (Attias et al., 2016;
655 Plaza-Faverola et al., 2010).

656
657 Senger et al. (2010) compiled a large database of geophysical and geotechnical borehole data for a
658 resource evaluation of the Norwegian Sea gas hydrate prospect. Their method was based on a
659 stochastic approach and closely followed that of conventional hydrocarbon prospect evaluation. The
660 calculated in-place volume has a large uncertainty, primarily due to the lateral variations in reservoir
661 parameters. Senger et al. (2010) estimated that the prospect (both hydrate and free-gas zones) contains
662 625 GSm^3 of gas. The amount of gas is significant compared to conventional hydrocarbon reservoirs
663 in the Norwegian Sea (e.g. the Ormen Lange field with about 439 GSm^3). However, the resource
664 density is rather low, so future economic exploitation is unlikely.

665

666 **6. Offshore Ireland**

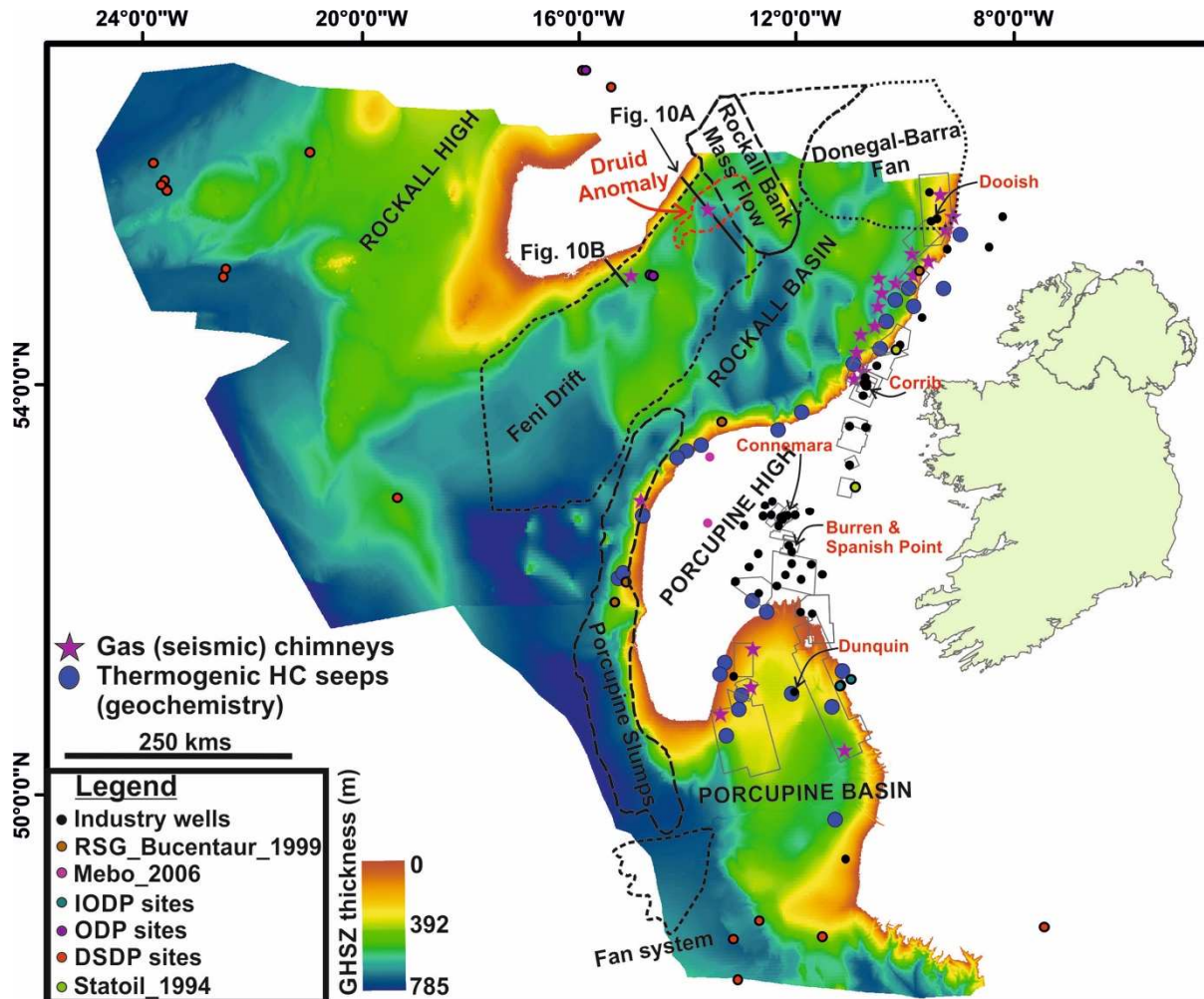
667 6.1 Geological Setting

668 The continental margin offshore Ireland bears the imprints and structures resulting from Variscan,
669 Caledonian and older orogenic events (Naylor and Shannon, 2011). The nature of the basement
670 successions, together with their inherent lineaments and structural fabrics, had a major influence on
671 the location and structural segmentation of the basins. Basins of various geometries, sizes and ages,
672 filled with thick Cenozoic successions, occur in the western Irish Atlantic shelf, in water depths of
673 400 m to more than 4500 m. Four kilometres of Cenozoic strata occur in the Porcupine Basin and up
674 to 2 km have been identified on seismic profiles in the Rockall Basin (Shannon et al., 1993). Fluid
675 flow within the basins is likely to have been controlled by the overall basin geometry and by the
676 distribution and linkage of permeable strata with fault systems and unconformities. Active petroleum
677 systems in the Rockall and Porcupine basins have been documented by oil and gas exploration since
678 the 1970s.

679

680 Potential source rocks include the Upper Carboniferous, Middle and Upper Jurassic successions,
681 which are generally mature throughout these basins. The Cretaceous and Cenozoic successions also
682 have some potential for oil and gas generation. The Kimmeridgian succession (Upper Jurassic) is a
683 good proven source rock that is well distributed in the Porcupine Basin. It has total organic carbon
684 (TOC) values of 3 - 4%. The Lower Cretaceous succession has TOC values of 1.8 – 2.7% (Naylor and
685 Shannon, 2011). The Dooish gas condensate discovery on the eastern margin of the Rockall Basin

686 demonstrates the presence there of a thermogenic petroleum system. Middle Jurassic lacustrine
 687 mudstone is anticipated as a potential source as in the Porcupine Basin. Other source rocks are the
 688 Lower Cretaceous with TOC values of 3-14%, and Albian lacustrine mudstones with TOC values of
 689 2.04% (Hitchen, 2004).



690 Figure 9: Calculated HSZ of Irish basins, for pure methane and 3.5% salinity and using seabed
 691 temperature from a compilation of oceanographic data and a geothermal gradient of 30-35°C/km (Roy
 692 et al., 2017). Also shown are locations of 3D seismic cubes, boreholes, gas chimneys, hydrocarbon
 693 (HC) seeps, and proven hydrocarbon systems (text in red).
 694
 695

696 6.2 Hydrate Occurrence

697 High resolution bathymetric data (100 m resolution), seabed temperature from 4760 CTD casts, and
 698 geothermal data from four boreholes have been used to calculate the HSZ offshore western Ireland
 699 (Roy and Max, 2018; Fig. 9). An extensive set of geophysical and geological data was integrated for
 700 the assessment of lithology, migration pathways of natural gas-saturated water in the form of chimney
 701 structures (Van Rensbergen et al., 2005b), presence of source rocks or conventional reservoirs, as well
 702 as host rocks for hydrate within its stability zone. A brief summary of the datasets used is provided
 703 below, with locations shown in Fig. 9:

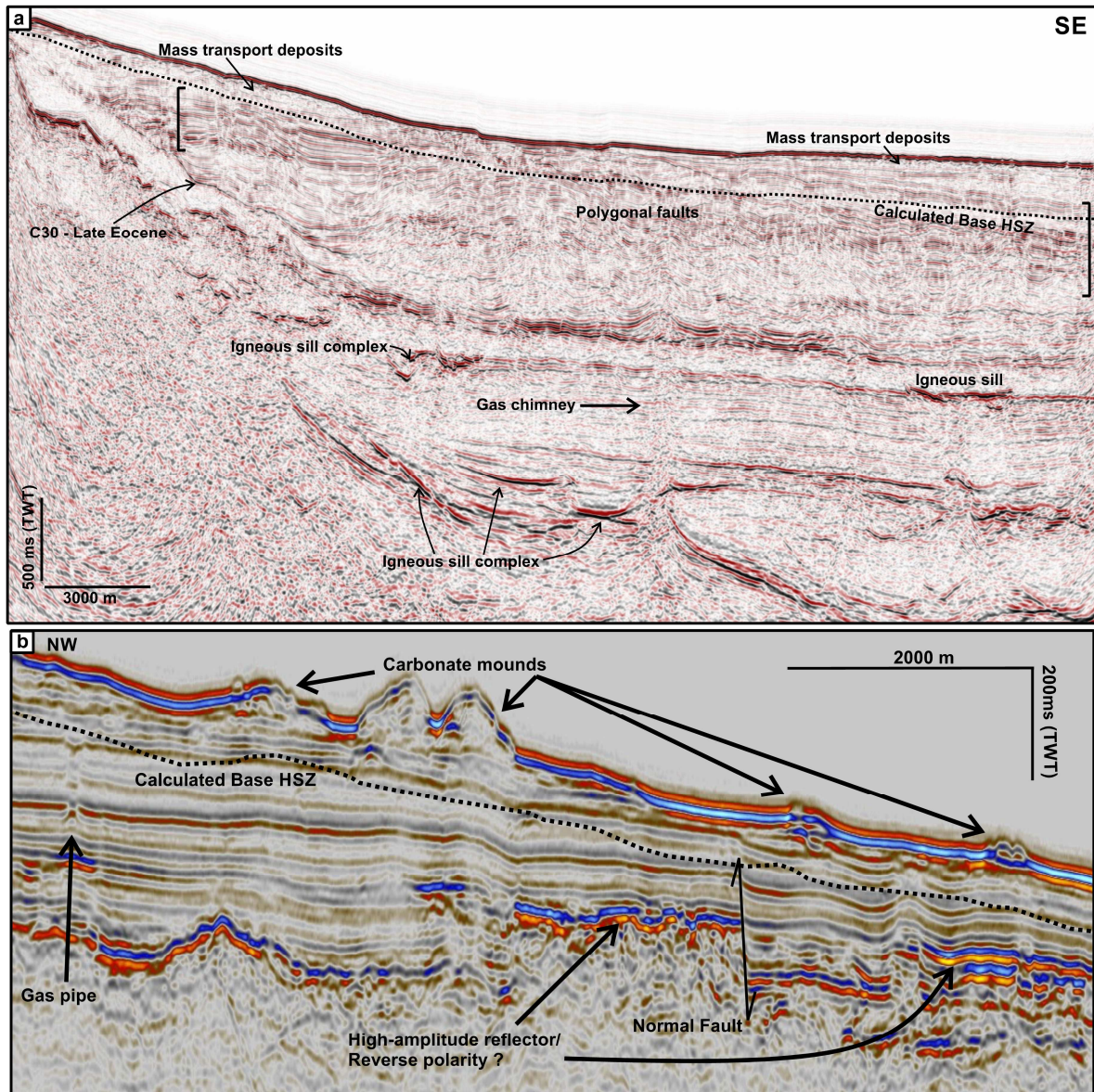
- 704 a) Industry scale exploration data: 31 2D multichannel seismic surveys, 11 3D seismic cubes,
705 and 18 exploration wells drilled within the HSZ.
- 706 b) Scientific drilling campaigns: Integrated Ocean Drilling Programme (2 sites), Ocean Drilling
707 Programme (2 sites) and 12 Deep Sea Drilling Project (12 sites) within the HSZ.
- 708 c) Shallow drilling campaigns: Statoil 1994 (1 site), Rockall Study Group Bucentaur 1999 (3
709 sites), and Mebo 2006 (1 site).

710 The HSZ extends up to 645 m below the seafloor in the Rockall Basin, and 784 m in Porcupine Basin
711 (Fig. 9). Fluid escape features, gas chimneys, bright spots indicating shallow gas accumulations, and
712 faults that act as pathways for fluid migration, have been interpreted above potential source rocks and
713 active petroleum systems. Three types of depositional systems have been identified as potential hosts
714 for hydrate accumulations in Irish basins:

- 715 a) Mass transport deposits (MTDs): Slope failures are widespread along both the western and
716 eastern margins of the Rockall Basin. Sidescan sonar images show a broad interplay of along-
717 slope and downslope sediment transport, with sediment sourced from the northeastern margin
718 and redistributed by currents along the western margin (Unnithan et al., 2001). Along the
719 western margin, the Rockall Bank Mass Flow is a large, multi-phase submarine slope failure
720 comprising of several MTDs, with failure scarps extending over *c.* 6100 km². It lies upslope a
721 series of mass flow lobes covering *c.* 18,000 km² of the Rockall Basin seafloor (Elliott et al.,
722 2010). Low- to medium-porosity turbidites have been found in shallow gravity cores of the
723 lobes, which could be ideal hydrate reservoirs (Roy and Max, 2018).
- 724 b) Feni contourite drift: The Feni drift lies along the northwest flank of Rockall Basin, formed
725 under the influence of deep, geostrophic currents formed by intermittent overflows of Arctic
726 Intermediate Water from the Norwegian Sea. Sites 980 and 981 from ODP Leg 162 are
727 located on the Feni Drift sediments. It is predominantly composed of rapidly accumulated
728 nannofossil oozes with variable amounts of clay and silt. The lithology of Feni Drift is similar
729 to that of Blake Ridge sediments but bed differentiation may be better. Extensive fluid escape
730 features from deeper Lower Jurassic source rocks extend over an area \sim 2000 km², known as
731 the Druid Anomaly (Fig. 9). Gas chimneys terminate beneath polygonal faults observed partly
732 within the HSZ, which has an average thickness of 225 m (Roy and Max, 2017; Fig. 10).
- 733 c) Turbidite and contourite deposits: Isolated sand bodies, contourite furrows (erosional
734 features), and turbidite channel systems have been mapped from 3D seismic data within the
735 HSZ in the Porcupine Basin (Roy and Max, 2018). Associated gas chimneys and fault
736 systems mark upwelling fluid migration from deeper sources to these potential hydrate
737 reservoirs.

738 BSRs have not been identified in the Irish basins. A reason for the absence of a BSR in the available
739 seismic data could be that these data were processed to better identify deeper structural and

740 stratigraphic geological traps. The processing sequence may have obscured shallower structures.
 741 Various seismic amplitude anomalies (e.g., bright spots, seismic gas pipes and chimneys, reverse
 742 polarity) have been observed in close proximity to the calculated base of the HSZ (Fig. 10b). Possible
 743 BSRs have been documented within contourite deposits in the southern and central parts of Porcupine
 744 Basin, at water depths of 1500 - 2200 m (Roy and Max, 2018).



745 Figure 10: a) Seismic reflection profile showing gas chimney (part of the Druid anomaly) in the
 746 Rockall Basin, originating from potential source rock, with polygonal faults, sill complexes, mass
 747 transport deposits (Rockall Mass Flow), and C30 late Eocene unconformity (Roy et al., 2017). The
 748 extent of polygonal faults, which extend into the HSZ in the southeast, is shown by square brackets.
 749 These faults could act as potential fluid migration pathways for deeper fluids to reach the HSZ
 750 (interpolated from the grid of Fig. 9). b) Interpretation of suspected shallow gas accumulation
 751 (enhanced high-amplitude reflections) beneath the calculated base of HSZ, and fluid migration
 752 pathways such as gas pipes and normal faults in Rockall Basin. Locations are marked in Fig. 9.
 753
 754

755 **7. Northwest Iberian Margin**

756 7.1 Geological Setting

757 The northwest Iberia continental margin developed during the northward propagation of the North
758 Atlantic Ocean rift system (Boillot, 1995; Boillot et al., 1979; Pérez-Gussinyé and Reston, 2001).
759 Several extensional phases from the Triassic to the Early Cretaceous lead to a complex fault system
760 formed by north-south to northwest-southeast normal faults and northeast-southwest to east-west
761 transfer faults (Pinheiro et al., 1996; Wilson et al., 1989). North-south compression during the Alpine
762 orogeny resulted in the reactivation and partial inversion of previous rift structures and the generation
763 of new compressional structures (Murillas et al., 1990; Pinheiro et al., 1996; Vázquez et al., 2008).

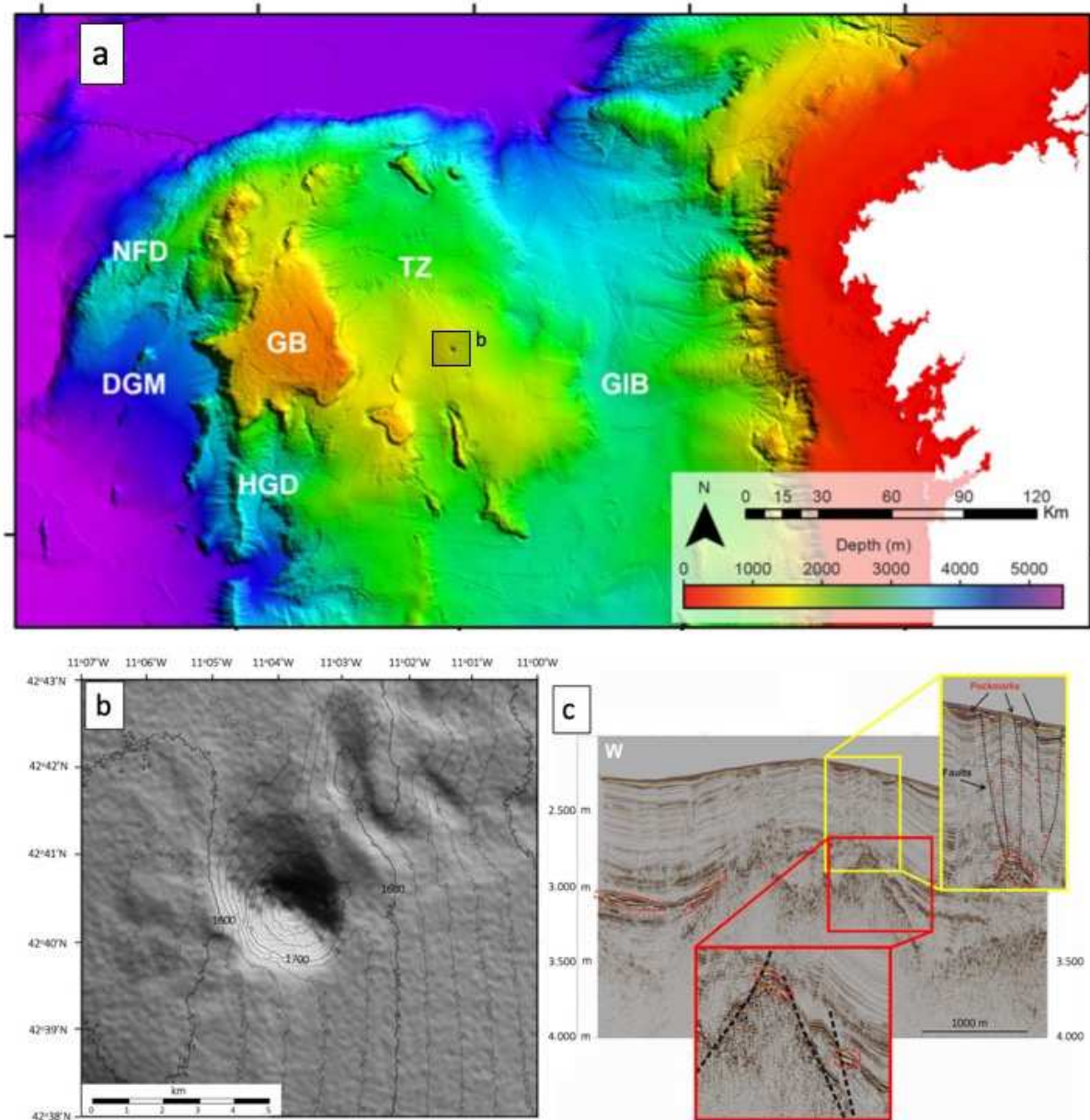
764

765 The present-day northwest Iberia continental margin is characterised by a roughly north-south, ~40
766 km wide continental shelf and a relatively steep slope down to ~2000 m water depth. Beyond the
767 continental slope, the continental margin can be divided into three main geomorphological provinces
768 (Fig. 11; Reston, 2005): 1) the Galicia Interior Basin (GIB); 2) the Western Banks – an area of
769 seamounts that includes the Galicia Bank; and 3) the Deep Galicia Margin (DGM). The sedimentary
770 cover ranges from 0 to 4 km, with maximum thickness in the Galicia Interior Basin depocenter
771 (Pérez-Gussinyé et al., 2003).

772

773 7.3 Hydrate Occurrence

774 The data available for determining the likelihood of methane hydrate stability and presence on the
775 northwest Iberia margin come from diverse sources of varying resolution. Bathymetry data with a
776 minimum 250 x 250 m resolution are publicly available on the EMODnet bathymetry data portal (
777 EMODnet Bathymetry Consortium, 2016). A higher resolution bathymetric grid (100 x100 m)
778 compiled by the Spanish Naval Hydrographic Institute has limited public availability (Druet et al.,
779 2018; Maestro et al., 2018; Somoza et al., 2014). Only two research cruises have been focused on
780 shallow gas occurrence there (Rey and Gran Burato Science Team, 2010, 2011). These cruises
781 acquired high-resolution multichannel and very-high-resolution single channel (3.5 kHz) seismic data
782 and multibeam data to characterise three giant pockmarks depressions in the Transitional Zone (Fig.
783 11) between the highly thinned crust of the Galicia Interior Basin and the relatively unthinned crust of
784 the Galicia Bank.



785

786 **Figure 11:** a) Bathymetry of the northwest Iberian Margin. GIB: Galicia Interior Basin, TZ:
 787 Transitional Zone, GB: Galicia Bank, NFD: Northwest Flank Domain, DGM: Deep Galicia Margin,
 788 HGD: Half-graben Domain. Note the three large circular structures in the Transitional Zone; b) Detail
 789 of the Gran Burato (GB) giant pockmark (after Druet, 2015) corresponding to grey square in a); c)
 790 Seismic line located south of the Gran Burato pockmark in b) showing how amplitude anomalies
 791 (circled in red) sourced fluid activity (after Ribeiro, 2011).

792

793 Evidence for shallow gas in the proximal northwest Iberia continental margin has been described
 794 since the early 2000s (Durán et al., 2007; Ferrín et al., 2003; García-García et al., 2003; García-Gil et
 795 al., 2015). However, the possibility of hydrate occurrence did not emerge until a decade later based on
 796 the presence of several seabed features related to fluid escape imaged in the Transitional Zone (Druet,
 797 2015; Ercilla et al., 2011; López Pérez et al., 2019; Ribeiro, 2011). Some of the fluid escape structures
 798 have a seafloor expression (e.g., pockmarks), while others were detected by seismic amplitude

799 anomalies. Pockmarks were identified with a wide range of size and depths, on almost all the seismic
800 profiles acquired in the Transitional Zone (Rey and Gran Burato Science Team, 2010, 2011; Ribeiro,
801 2011). The three biggest pockmarks, in water depths of 1600-1850 m, correspond to semicircular
802 depressions that have depths up to 375 m and diameters between 2 and 5 km. A detailed study of the
803 Gran Burato (Fig. 11b), the northernmost and largest pockmark in the Transitional Zone, showed
804 evidence for fluid (most likely gas) migration and accumulation in both deep and shallow
805 stratigraphic units (Ribeiro, 2011). Additionally, two fields of medium-size pockmarks with a density
806 of more than five pockmarks per square kilometer were described (Rey and Gran Burato Science
807 Team, 2011). Stratigraphic analysis of seismic data suggests that some these pockmarks are related to
808 middle Miocene to Quaternary sedimentary units. Some of the pockmarks still appear to be active
809 (Ribeiro, 2011). The most recent and intense fluid escape takes place in the northernmost sector. An
810 estimate of the HSZ based on the regional geothermal gradient suggests widespread hydrate stability
811 in the area (Rey and Gran Burato Science Team, 2011).

812
813 Various seismic amplitude anomalies (e.g., areas of seismic blanking, bright spots, chimney
814 structures) have been identified close to the pockmark fields and are interpreted as evidence of gas
815 presence within the sediments (Ribeiro, 2011). Fig. 11c shows high-amplitude anomalies on a
816 structural high that pinch out against faults. Pockmarks observed immediately above may result from
817 extensive structurally controlled fluid seepage via faults and fractures (Ribeiro, 2011). A high-
818 amplitude reflector that mimics the seabed was observed in some seismic profiles at the estimated
819 hydrate phase boundary depth, but the polarity inversion typically associated with BSRs could not be
820 identified, so its origin remains uncertain (Rey and Gran Burato Science Team, 2011).

821
822 Analysis of sediment samples from piston cores collected close to the Gran Burato were inconclusive
823 (Rey and Gran Burato Science Team, 2011). Some signs of liquefaction were observed in one piston
824 core, but no associated thermal anomalies were registered, though long core travel times may have
825 attenuated such anomalies. Also, no evidence for chlorinity anomalies or significant sulphate
826 depletion was reported (Rey and Gran Burato Science Team, 2010, 2011). Benthic fauna associated
827 with gas seepage were reported, although the observed species are not exclusive to these
828 environments.

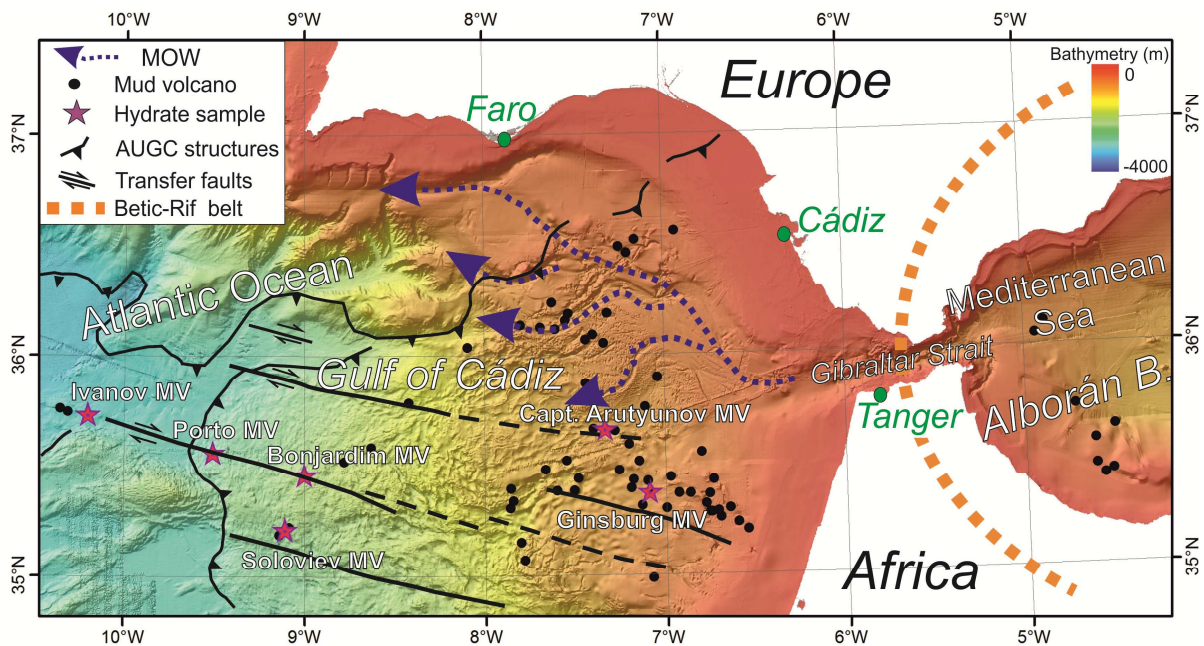
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830 **8. South Iberia and Northwest African Margin**

831 8.1 Geological Setting

832 The South Iberia and Northwest Africa margins are located in the context of the Betic–Rif orogen
833 either side of the Gibraltar Strait: the Gulf of Cádiz (Eastern Atlantic) and Alborán Sea basin
834 (Western Mediterranean) (Fig. 12). The Atlantic margins of the Gulf of Cádiz were formed during
835 Mesozoic rifting close to the boundary between the Central and North Atlantic. From the late

836 Oligocene to the early Tortonian, these margins were deformed by north-south convergence between
 837 the African and Eurasian plates due to the westward drift of the Alborán Domain and development of
 838 the Betic-Rif belt (Platt et al., 2003). Simultaneously the Alborán Basin was developed by extensional
 839 normal faulting and crustal thinning in the back-arc area of the Alborán Domain. Northwest-southeast
 840 convergence caused a post-Tortonian compressive regime that produced the progressive inversion of
 841 the basin, Betic-Rif range uplift, two sets of strike-slip faults, reverse faults and folds (Estrada et al.,
 842 2018; Martinez-Garcia et al., 2017). There was subsequent mud diapirism and related mud volcanism
 843 and the formation of pockmark fields (Pérez-Belzuz et al., 1997; Somoza et al., 2012), which occur
 844 mainly in the western part of the Alborán Basin (Pérez-Belzuz et al., 1997).



845
 846 Figure 12. Bathymetry of the South Iberia and Northwest Africa margins. Arrows mark flow
 847 directions of Mediterranean outflow water. Stars mark mud volcanoes (MV) at which hydrate has
 848 been sampled. Black dots mark other mud volcanoes. The boundaries of the Allochthonous Unit of
 849 the Gulf of Cádiz (AUGC) are modified from Medialdea et al. (2009). Black lines mark southwest
 850 Iberia Margin (SWIM) faults (dashed where discontinuous).

851
 852 In the Gulf of Cádiz, the westward migration of the Alborán Domain forced the emplacement of a
 853 large tectono-sedimentary allochthonous unit in the continental margin and oceanic realm of the Gulf
 854 of Cádiz, generally known as the allochthonous unit of the Gulf of Cádiz (AUGC) (Medialdea et al.,
 855 2009). The AUGC is responsible for diapirism of huge volumes of mud and salt of Triassic units and
 856 also for under-compacted early to middle Miocene plastic marls and shales (Fernandez-Puga et al.,
 857 2007; Maldonado et al., 1999; Medialdea et al., 2009). Numerous seabed fluid escape structures result
 858 from this diapirism, including mud volcanoes, of which some bear hydrate (León et al., 2012;
 859 Mazurenko et al., 2002; Pinheiro et al., 2003; Somoza et al., 2003; Van Rensbergen et al., 2005a),
 860 hydrocarbon-derived authigenic carbonate (HDAC)-bearing chimneys (Diaz-del-Rio et al., 2003;
 861 Magalhaes et al., 2012; Palomino et al., 2016) and pockmarks (Baraza and Ercilla, 1996; León et al.,

862 2014; León et al., 2010; León et al., 2006). The distribution of these fluid migration and escape
863 structures is also related to the arcuate wedge and the west-northwest to east-southeast SWIM
864 transcurrent fault system (Fig. 12; Hensen et al., 2015). The deeper mud volcanoes (2500-4500 m
865 water depth), located in the Southwest Iberia Margin segment of the Gulf of Cádiz area, are closely
866 linked to the presence of the active strike-slip SWIM faults, which provide pathways for deep-seated
867 fluids sourced from oceanic crust older than 140 Ma (Hensen et al., 2015). A local and discontinuous
868 BSR has been observed only in the upper slope (between 200 and 400 m water depth) on the Iberian
869 margin of the Gulf (Casas et al., 2003) and within a mud volcano in the Moroccan slope (Depreiter et
870 al., 2005). Hydrate and hydrocarbon gases sampled from mud volcano sediments include both
871 microbial and thermogenic components (Mazurenko et al., 2002; Stadnitskaia et al., 2006).

872

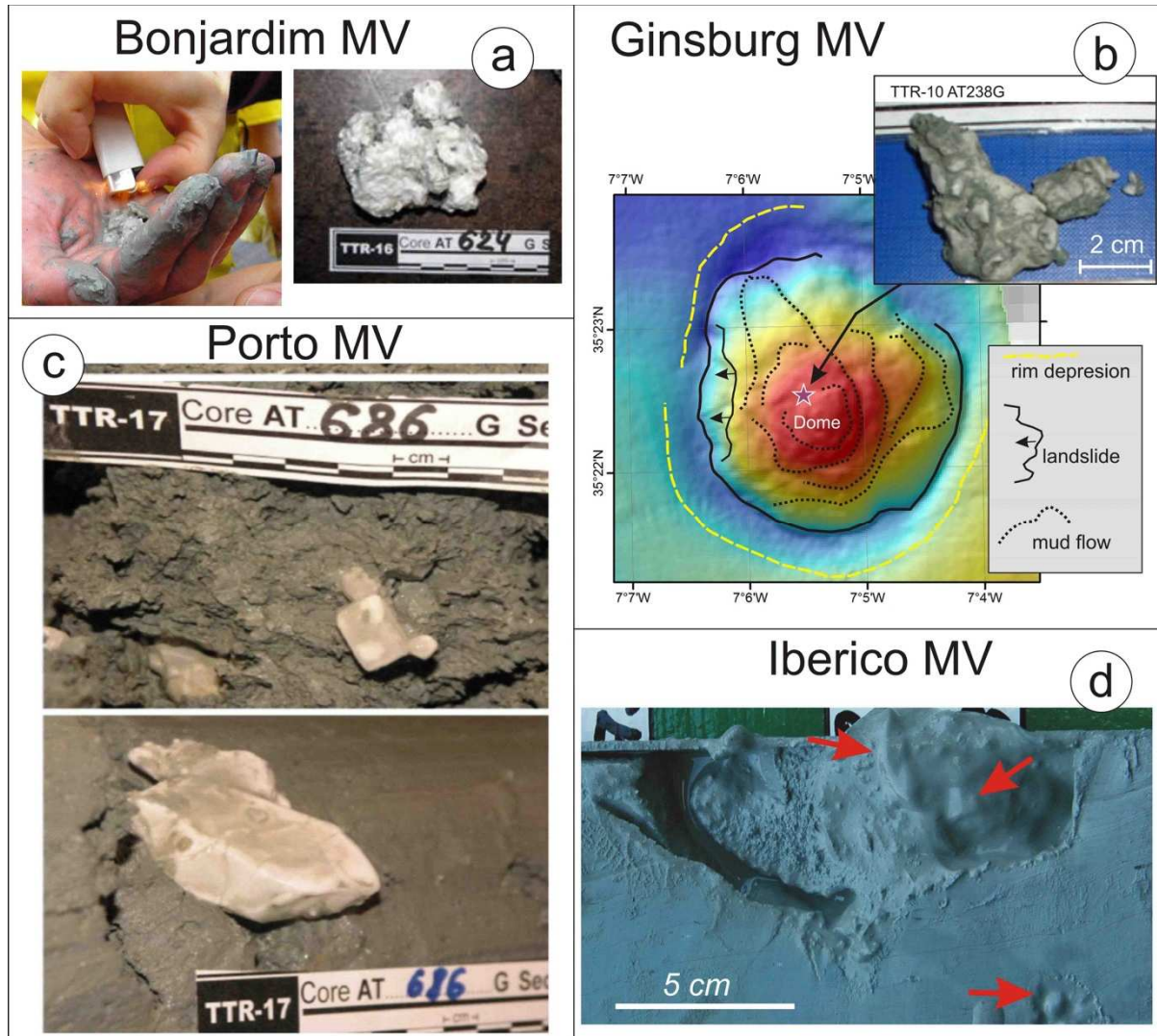
873 8.2 Hydrate Occurrence

874 Direct evidence for hydrate in the Gulf of Cádiz has been detected only in association with the mud
875 volcanoes. The first sample was recovered in 1999 at the Ginsburg mud volcano (Gardner, 2001;
876 Mazurenko et al., 2002). Subsequent work confirmed the presence of hydrate in six other mud
877 volcanoes at 930-4500 m water depth (Hensen et al., 2015; Mazurenko et al., 2002; Pinheiro et al.,
878 2003; Fig. 12). Hydrate appears in various morpho-stratigraphical types, including a tabular shape of
879 irregular thickness (up to 1-2 mm), forming layers within the sediment; or isometric sub-rounded
880 aggregates or individual clast-like occurrences, from millimetre size to several centimetres. The
881 biggest samples (> 5cm) have been recovered in the Porto and Michael Ivanov mud volcanoes
882 (Hensen et al., 2015). They comprise disseminated clasts inside a homogeneous mud breccia of grey
883 or dark grey color, saturated in gas and with a porous structure resulting of degasification. In some of
884 the mud volcanoes (e.g. Ginsburg and Captain Arutyunov), based on chlorinity anomalies in sediment
885 cores, hydrate content can reach 3-16% of the sediment volume and 5-31% of the pore space volume
886 (Mazurenko et al., 2002). Hydrocarbon gases from gravity cores collected from Ginsburg mud
887 volcano indicate allochthonous natural gases of thermogenic origin, with 81% methane and 19%
888 higher hydrocarbons (Mazurenko et al., 2002; Stadnitskaia et al., 2006). The ratio iso-C4/n-C4 points
889 to focused fluid flow as the principal mechanism of gas migration (Stadnitskaia et al., 2006).
890 Differences in the composition of hydrocarbon gases between the deep Portuguese margin and the
891 Atlantic Morocco middle continental slope suggest two groups with distinctive fluid venting
892 environments and geochemical behavior/properties of migrating fluids, resulting from a complex of
893 secondary migrated, microbially altered and mixed hydrocarbons (Stadnitskaia et al., 2006).

894

895 Indirect evidence for hydrate has been found in other mud volcanoes and mud mounds in the Gulf of
896 Cádiz. The most common indirect evidence is liquefied and degassing structures in the mud breccia
897 sediments (Fig. 13). These structures have been detected in most mud volcanoes below 1000 m water
898 depth and in some carbonate mounds such as Cornide. In the Alborán Sea, degassing structures have

899 been detected only in one gravity core from the Carmen mud volcano. Coherent reversed-polarity
 900 reflections beneath the slopes of mud volcanoes, interpreted as BSRs have been detected in the
 901 Atlantic Moroccan margin below Mercator mud volcano (Depreiter et al., 2005). Similar reflections
 902 that are quasi-parallel to the seafloor and interpreted as BSRs have been detected in seismic profiles
 903 from the Portuguese continental upper slope seaward the city of Faro. Finally, the presence of
 904 chloride ion concentrations below 450 mM, indicating the presence of dissociated hydrate (Hesse and
 905 Harrison, 1981), has been detected in the hydrate-bearing mud volcanoes, as well as in the Yuma,
 906 Carlos Ribeiro and Olenin mud volcanoes, where hydrate was not recovered (Mazurenko et al., 2002).



907

908 Figure 13. Direct and indirect hydrate evidence of the South Iberia and Northwest Africa margins. a)
 909 Hydrate sample from the Bonjardim mud volcano (AT624 from Akhmetzhanov et al., 2008); b)
 910 Bathymetry and geological interpretation of the Ginsburg mud volcano (modified from Toyos et al.,
 911 2016) with the location of the first hydrate sample recovered in the Gulf of Cádiz (AT238G from
 912 Kenyon et al., 2001); c) Hydrate crystals from a gravity core at Porto mud volcano (Ivanov et al.,
 913 2010); d) Liquefied structures (red arrows) inferred to represent hydrate dissociation in a gravity core
 914 from Ibérico mud volcano (Leon, 2007).

915

916 Thus, hydrate in the Gulf of Cádiz seems to be present in localised deposits and hosted in fine-grained
917 sediments with low permeability, although the thickness and extent of hydrate present are poorly
918 known. This type of occurrence cannot be considered to be of significant resource potential. No
919 hydrate has been detected in any other geological features, such as pockmarks in the Gulf of Cádiz,
920 nor in the Estremadura Spur of the west Iberia margin (Duarte et al., 2017). Hydrate indications are
921 also absent in the sandy or muddy contourite deposits of the continental slope of the Gulf of Cádiz.
922 The lack of hydrate evidence in pockmarks could also be related to the insufficient data collected on
923 these sites. HDACs recovered in pockmarks show an isotopic composition (depletion in $\delta^{13}\text{C}$ and
924 enrichment in $\delta^{18}\text{O}$) compatible with possible past massive hydrate dissociation episodes (Diaz-del-
925 Rio et al., 2003).

926
927 Moreover, the BSRs that were identified occur only locally, without regional continuity, and in close
928 association with fluid escape areas (Casas et al., 2003; Depreiter et al., 2005). In multichannel seismic
929 profiles, areas of blanking and amplitude anomalies below pockmark fields, collapse structures and
930 mud volcanoes reflect the presence of fluids (very possibly hydrocarbon fluids) in the sediment
931 column (Medialdea et al., 2009). Suitable reservoirs for hydrate, comprising thick sandy contourite
932 deposits generated by the Mediterranean outflow water (MOW), exist in the Gulf of Cádiz at 400-
933 1200 m water depth. However, this water mass warms the seafloor and results in variation of the
934 hydrate stability field through time. Global sea-level changes and subsequent episodic warming by the
935 MOW undercurrents are the most plausible scenarios for massive hydrate dissociation in the Gulf of
936 Cádiz during the Quaternary (León et al., 2010). Thus, hydrate could extend beyond the seabed fluid
937 escape structures where it has been observed, and ultimately the amount of hydrate present is
938 unknown.

939
940 Although hydrate has not been sampled in the mud volcanoes of the Alborán Sea, their presence has
941 been proposed due to indirect evidence from some mud volcano structures (e.g., Blinova et al., 2011).
942 Here, hydrate occurrence was inferred from the large gas release during core sampling. Pore water
943 geochemistry provided further evidence, with a 160 to 600 mMol chlorinity anomaly. The gas was
944 inferred to be thermogenic and from a deep (around 5 km) source (Blinova et al., 2011).

945

946 **9. Eastern Mediterranean**

947 9.1 Geological Setting

948 The Eastern Mediterranean Sea (Fig. 14) is a diverse composite of tectonic elements, which evolved
949 through the Mesozoic formation and fragmentation of the northern passive margin of Gondwanaland
950 and subsequent collision with Eurasia to form a subduction and accretionary complex (e.g.,
951 Garfunkel, 2004). An increasing supply of clastic sediments since the Oligocene formed the extensive

952 present-day Nile fan, extending into the Herodotus and Levant basins and reaching thicknesses of >8
953 km (Macgregor, 2012). Restricted connectivity with the Atlantic Ocean during the Messinian salinity
954 crisis resulted in the deposition of evaporites across the Mediterranean basin and accumulation of ~2
955 km of salt within the Levant and Herodotus basins (CIESM, 2008).

956
957 The Eastern Mediterranean Sea is expected to host a significant amount of hydrate (e.g., Merey and
958 Longinos, 2018) because large areas of the seabed are located within the HSZ (Fig. 1). The geological
959 variability of this region offers a variety of potential hydrate depositional environments. The deep-
960 water temperature ranges between 13 and 14 °C (e.g., Zavatarelli and Mellor, 1995), so that hydrate is
961 only stable at water depths of >1000 m (Praeg et al., 2011). The geothermal gradient varies
962 significantly between 20-30 °C/km in the Nile fan and associated deep basins to the south and ~60
963 °C/km in the Aegean (e.g., Makris and Stobbe, 1984), resulting in a variable sub-seafloor depth of the
964 base HSZ across the area. The Eastern Mediterranean is extremely oligotrophic (Krom et al., 2004).
965 The major potential sources for hydrocarbon formation are Tethyan deposits, late Messinian shallow
966 water deposits and Miocene to recent sapropels and other organic-rich intervals (e.g., Merey and
967 Longinos, 2018).

968

969 9.2 Hydrate Occurrence

970 Multiple observations indicate the availability of gas, required for the formation of hydrate, across the
971 seafloor. In particular, numerous mud volcanoes are present, primarily along the accretionary
972 complex and to a lesser degree in the Nile fan (e.g., Mascle et al., 2014; Zitter et al., 2005). Mud
973 volcanoes in the Olimpi Field and at Anaximander Seamount exhibit gas seeps and broad degassing
974 areas, with associated chemosynthetic fauna and authigenic carbonates (Aloisi et al., 2000; Zitter et
975 al., 2005). In both locations, pockmarks have been identified and some of these are filled with brines
976 characterized by high gas content (Dimitrov and Woodside, 2003). The gas seeps have clear
977 thermogenic signatures, indicating deep-rooted fluid expulsion sources (e.g., Pape et al., 2010). Away
978 from mud volcanoes, an abundance of gas, predominantly microbial methane (e.g., Römer et al.,
979 2014; Rubin-Blum et al., 2014), is indicated by a multitude of deep sea seafloor gas seepage features
980 that have been identified over the last two decades across the Nile fan (Dupre et al., 2010; Loncke et
981 al., 2004), Levant basin (Tayber et al., 2019) and Eratosthenes Seamount (Mitchell et al., 2013).
982 These features include gas bubbling, pockmarks, and authigenic carbonates at the seafloor, and a
983 variety of seismic reflection anomalies beneath the seabed, including bright spots and seismic
984 blanking. The scope of known seepage is continuously expanding as new data become available,
985 providing further evidence for the potential for hydrate formation.

986

987 To date, hydrate has been sampled only in several mud volcanoes of the accretionary complex,
988 starting in the Anaximander Seamount region (Fig. 14). These include the Kula mud volcano

989 (Woodside et al., 1997), the nearby Amsterdam, Kazan, Athina, and Thassaloniki mud volcanoes
990 (Lykousis et al., 2009; Pape et al., 2010; Perissoratis et al., 2011), and those in the Olimpi field
991 offshore Crete, including the Napoli, Milano, Maidstone and Moscow mud volcanoes (Fig. 14; e.g.,
992 Aloisi et al., 2000). Most hydrate samples are within predominantly relatively fine muddy sediments.
993 In most cases the presence and dissolution of hydrate was indicated by the soupy texture of the
994 sampled sediments (e.g., Lykousis et al., 2009) or their signatures in pore water chlorinity and
995 chemistry (e.g., de Lange and Brumsack, 1998a; Pape et al., 2010).

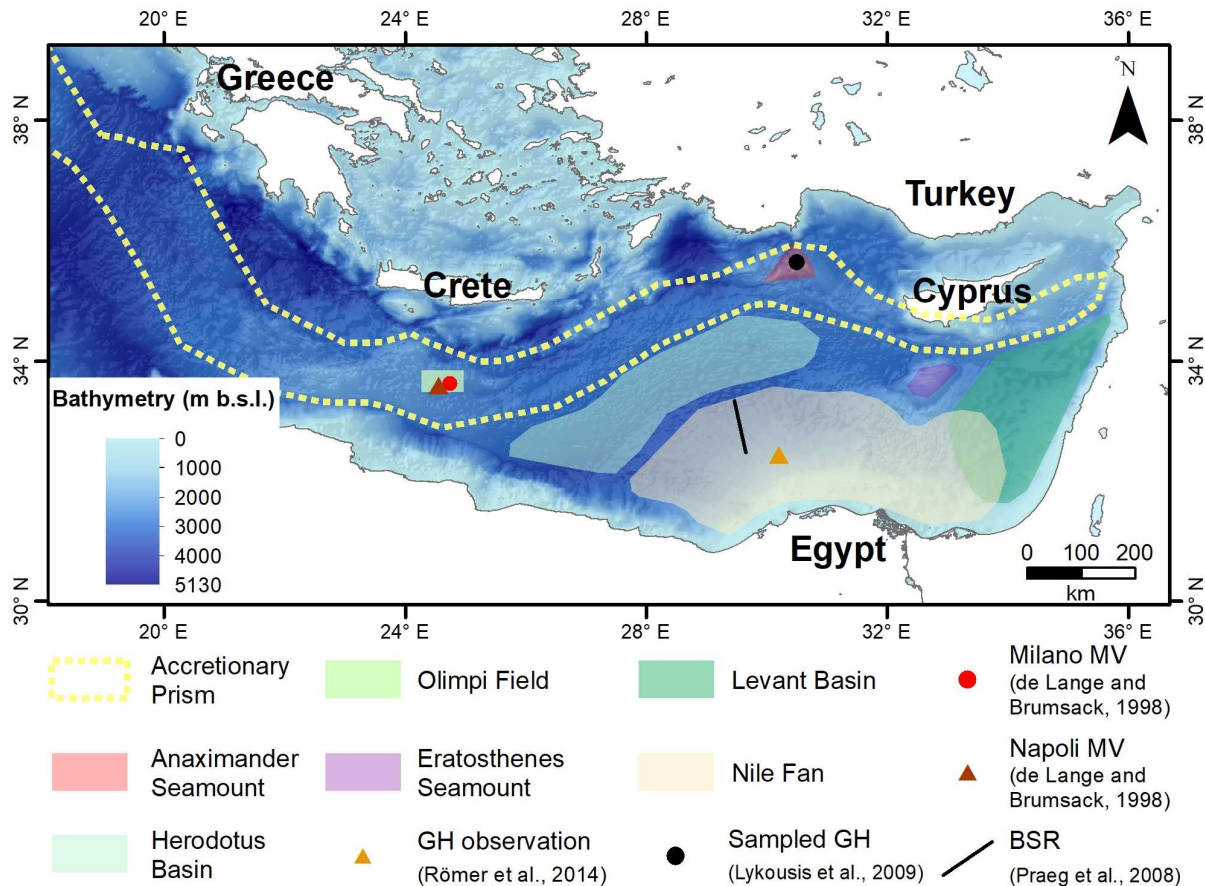
996
997 Analysis of sediments collected at the Mediterranean Ridge (ODP Leg 160, Site 971) suggests locally
998 massive hydrate occurrence at depths of 1 to over 40 m below seafloor across the summit of Milano
999 mud volcano (de Lange and Brumsack, 1998a). Based on a porosity of 60% to 40% (ODP Leg 160,
1000 hole 970A), the total amount of methane stored in this mud volcano as hydrate and free gas equal is
1001 estimated to be $5 \times 10^9 \text{ m}^3$ (De Lange and Brumsack, 1998b). In contrast, hydrate samples retrieved at
1002 Kazan mud volcano had a mm-scale rice-like appearance. Those from the summit of Amsterdam mud
1003 volcano occurred as several-cm scale flaky lumps resembling compacted snow, estimated to occupy a
1004 volume fraction of 16.7% within the sediment interval between the sulphate base and the maximum
1005 sampling depth of 2.5 m (Pape et al., 2010). This estimate is based on the analysis of four pressurized
1006 near-surface sediment cores (following e.g., Heeschen et al., 2007). In addition, pore-water analysis
1007 was used to assess the upper limit of hydrate stability. Both of the above hydrate morphologies were
1008 found on the Thessaloniki mud volcano, but the estimated volume fraction in a single 70-cm
1009 autoclave core was only 0.7% (Perissoratis et al., 2011). Lykousis et al. (2009) and Perissoratis et al.
1010 (2011) note that on Thassaloniki mud volcano, located at about 1260 m water depth, methane hydrate
1011 is present mostly just below the calculated upper limit of the HSZ. Thus, hydrate may dissociate due
1012 to small increases in temperature or decreases in pressure or salinity, which might occur due to
1013 climate change or local sediment transport.

1014
1015 In spite of the broad coverage of the Eastern Mediterranean by 2D and 3D commercial and academic
1016 seismic data, only a single observation of a BSR has been reported (Fig. 14; Praeg et al., 2008; Praeg
1017 et al., 2011). The suggested BSR appears as a discontinuous negative polarity reflection, 220-330 ms
1018 below the seafloor at water depths of 2000–2500 m on the distal part of the western deep sea Nile fan.
1019 If a mean seismic velocity of 1.6-1.8 km/s is assumed above the reflection, its depth agrees well with
1020 the modelled base of the HSZ (Praeg et al., 2017). Direct indications of hydrate stability, and of the
1021 presence of gas within the HSZ, in the Nile deep sea fan were provided by Römer et al. (2014). They
1022 observed formation of hydrate within a funnel during the collection of gas emitted from the seafloor.
1023 In addition, hydrate coating formed on ascending bubbles and dissolved below the modeled top of the
1024 HSZ. This latter result was supported by echo-sounder imaging. Geochemical analyses of vented gas

1025 suggest that it predominantly originates from microbial methanogenesis, with traces of thermogenic
 1026 input (Römer et al., 2014).

1027

1028 Based on a statistical analysis of a large 3D dataset covering a significant portion of the Levant basin,
 1029 Tayber et al. (2019) suggest that observed scattered high-amplitude reflectivity there marks a pseudo
 1030 BSR, representing the presence of hydrate and associated underlying gas within localised sandy
 1031 buried channel systems. Tayber et al. (2019) estimated the hydrate volume associated with these
 1032 presumed accumulations at ~ 100 Tcf (~ 3000 GSm³) and its carbon content at ~ 1.5 Gt.



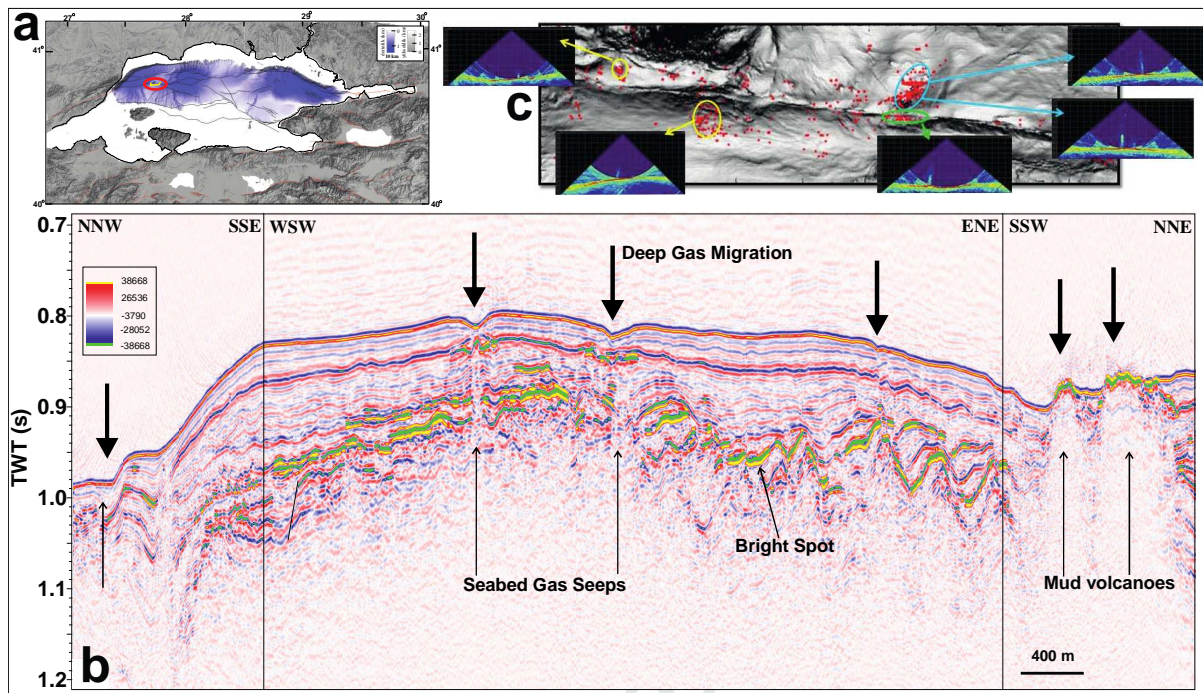
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1040 10. Sea of Marmara

1041 10.1 Geological Setting

1042 The Sea of Marmara is a pull-apart basin linking the onshore North Anatolian Fault with more
 1043 distributed extensional deformation in the Aegean. The current basin geometry appears to have
 1044 formed since 5 Ma by the rotation of several lithospheric blocks (Armijo et al., 1999). The basin
 1045 reaches a depth of over 1300 m and is subdivided into three sub-basins, from west to east named the
 1046 Tekirdağ, Central and Çınarcık basins, separated by basement highs named the Western and Central

1047 High, respectively (e.g., Le Pichon et al., 2001). It has been extensively studied over the past two
 1048 decades because of the hazardous active fault system that crosses its centre.



1049 Figure 15: a) Faults, bathymetry and topography of the Sea of Marmara. Bathymetry is from Rangin
 1050 et al. (2001) and faults from Sorlien et al. (2012). Red circle shows the study area and yellow line
 1051 inside shows the location of the seismic profile in b). b) Seismic reflection profile showing evidence
 1052 of shallow gas (Sarıtaş et al., 2018). Thick black arrows show gas seeps to seabed. The amount of gas
 1053 seeps is the highest at mud volcano area. Hydrate of thermogenic origin is sampled in the mud
 1054 volcanoes on the western high. High amplitude and reverse polarity bright spots are formed due to gas
 1055 accumulations. c) Seabed morphology of the central Sea of Marmara calculated from 3D seismic data
 1056 with red dots showing gas flares (Sarıtaş, 2013). Yellow circles mark gas seeps from pockmarks, blue
 1057 circle marks seeps from mud volcanoes and green circle marks seeps from the North Anatolian Fault.
 1058
 1059

1060 10.2 Hydrate occurrence

1061 Only small areas of the Sea of Marmara are deep enough to fall within the methane HSZ (Fig. 1).
 1062 However, hydrate has been sampled directly (Bourry et al., 2009) on the Western High, where
 1063 indications of sub-seabed fluid escape have been widely observed in seismic profiles around the North
 1064 Anatolian Fault system (e.g., Sarıtaş et al., 2018; Thomas et al., 2012; Fig. 15). Oil seeps have also
 1065 been observed (Crémière et al., 2012). Unequivocal BSRs have not been observed, but high-
 1066 amplitude reflections with reversed polarity that roughly mimic the seabed were clearly imaged in 2D
 1067 and 3D high-resolution multichannel seismic reflection data (e.g., Thomas et al., 2012). The
 1068 reflections do not cross-cut sedimentary strata, which also roughly parallel the seabed, so they may or
 1069 may not mark the base of the HSZ. They are similar to reflections seen in the Sorokin Trough in the
 1070 Black Sea (Krastel et al., 2003). Mud volcanoes, zones of seismic blanking and chimneys reaching the
 1071 seabed were also clearly imaged, suggesting the presence of abundant free gas in the shallow
 1072 sedimentary column.
 1073

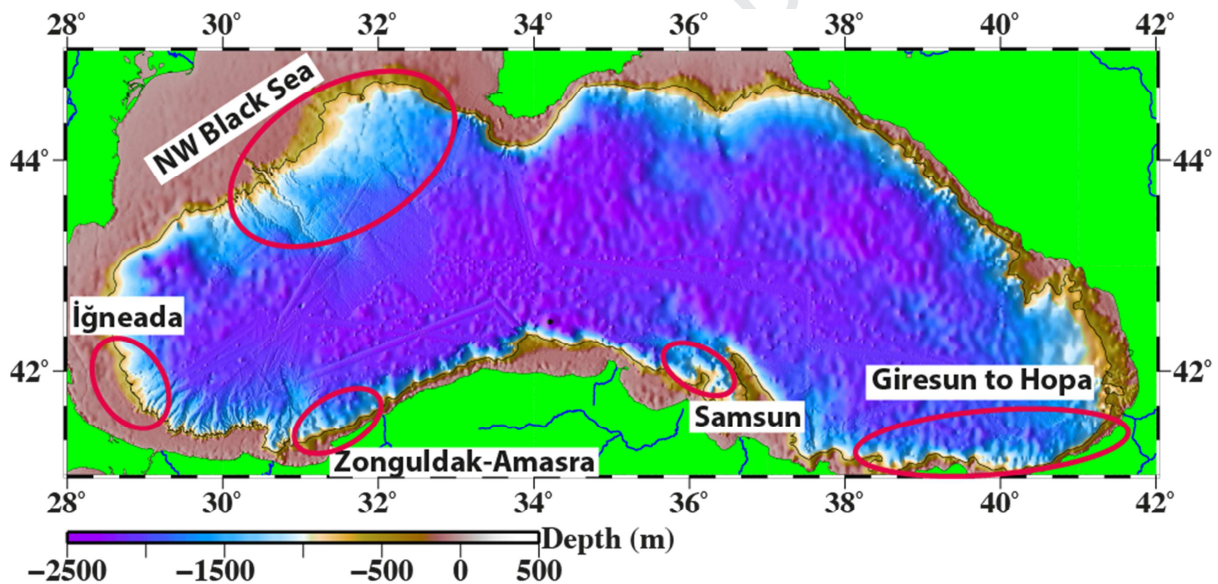
1074 Gas sampled from hydrate and bubble plumes was predominantly methane, but ethane, propane and i-
 1075 butane were also present, indicating a thermogenic source (Bourry et al., 2009). This thermogenic gas
 1076 may have migrated into shallow sediments via the North Anatolian Fault system from Oligocene to
 1077 Eocene reservoirs like those in the Thrace basin. Based on the gas compositions observed, both
 1078 structure I and structure II hydrate may be present.

1079

1080 **11. Black Sea**

1081 11.1 Geological Setting

1082 The Black Sea (Fig. 16) is a semi-isolated extensional basin with a maximum water depth of 2212 m.
 1083 Its deep waters (87% of the total volume) form the largest anoxic, hydrogen sulphide and methane
 1084 reservoirs in the world. The amount of dissolved methane contained in the basin (96 Tg) is 2.4-6
 1085 times greater than the global annual geological methane contribution to the atmosphere (Reeburgh et
 1086 al. 1991). 91% of its seafloor is within the range of hydrate stability (Vassilev and Dimitrov, 2002),
 1087 making the Black Sea an interesting target for a European hydrate field study.



1088

1089 Figure 16: Bathymetry of the Black Sea (Smith and Sandwell, 1997) with study areas described in the
 1090 text.

1091

1092 The Black Sea basin is generally thought to have formed in a back-arc environment because of its
 1093 spatial association with subduction of both the Paleo- and Neo-Tethys oceans (Letouzey et al., 1977).

1094 The timing and style of this opening history remain controversial, partly because the thick sediment
 1095 cover means that the oldest sedimentary fill has not been drilled (e.g., Nikishin et al., 2015;

1096 Zonenshain and Le Pichon, 1986). The Black Sea is subdivided into eastern and western basins

1097 separated by the Mid Black Sea High, a SW-NE system of buried basement ridges (e.g, Nikishin et

1098 al., 2015). Sediments in the Western basin may reach a thickness of up to 19 km (Nikishin et al.,

1099 2003). They include 4-5 km of folded organic-rich Maikopian deposits (Oligocene to lower Miocene)

1100 and 2-3 km of Cenozoic deposits (e.g., Finetti et al., 1988; Nikishin et al., 2015), which become
1101 thinner or disappear on the basin margin. Sediments in the eastern basin are thinner – perhaps only 8-
1102 9 km (Shillington et al., 2008).

1103

1104 11.2 Hydrate occurrence in the western Black Sea

1105 11.2.1 Offshore Romania and Bulgaria

1106 The northwestern Black Sea forms the transition zone between the Moesian Platform in the west,
1107 Scythian Platform in the north and the Western Black Sea Basin in the southeast. Structural styles of
1108 the Moesian and Scythian Platforms, which correspond to the Bulgarian and Romanian-Ukrainian
1109 EEZs, are significantly different. The former is quite structured and features normal faults with tilted
1110 blocks, while the latter is a mosaic of structural styles, with mainly Miocene gravity-driven thrusting,
1111 folding, toe-thrust and growth and tectonic deformation (Bega and Ionescu, 2009).

1112

1113 The northwest margin of the Black Sea (Fig. 17) is made up of the two largest and thickest organic-
1114 rich fan complexes in the Black Sea, the Danube and Dniepr fans, built up by the rivers Danube,
1115 Dniepr, Dniestr and Bug. Sediment deposition and the evolution of these fan systems has been
1116 controlled by climate and sea-level change (e.g., Ryan et al., 1997). The Danube and Dniepr fans
1117 developed from a significant stack of paleo-channels and levee deposits (Popescu et al., 2001;
1118 Winguth et al., 2000). Periodic seabed anoxia made conditions favourable for gas generation, as
1119 documented by the presence of more than 3000 gas plumes in the water column (Egorov et al., 2011),
1120 arranged in a circum-Black-Sea belt of gas flares. The majority of flares occur in water depths
1121 shallower than 665 m, which marks the present-day upper limit of the gas hydrate stability zone in the
1122 Black Sea. Exceptions are the underwater mud volcanoes, generally located in deeper waters, which
1123 can expel significant amounts of fluids, including methane. However, only 1.9% of the total methane
1124 escape from the seafloor reaches the atmosphere (Egorov et al., 2011).

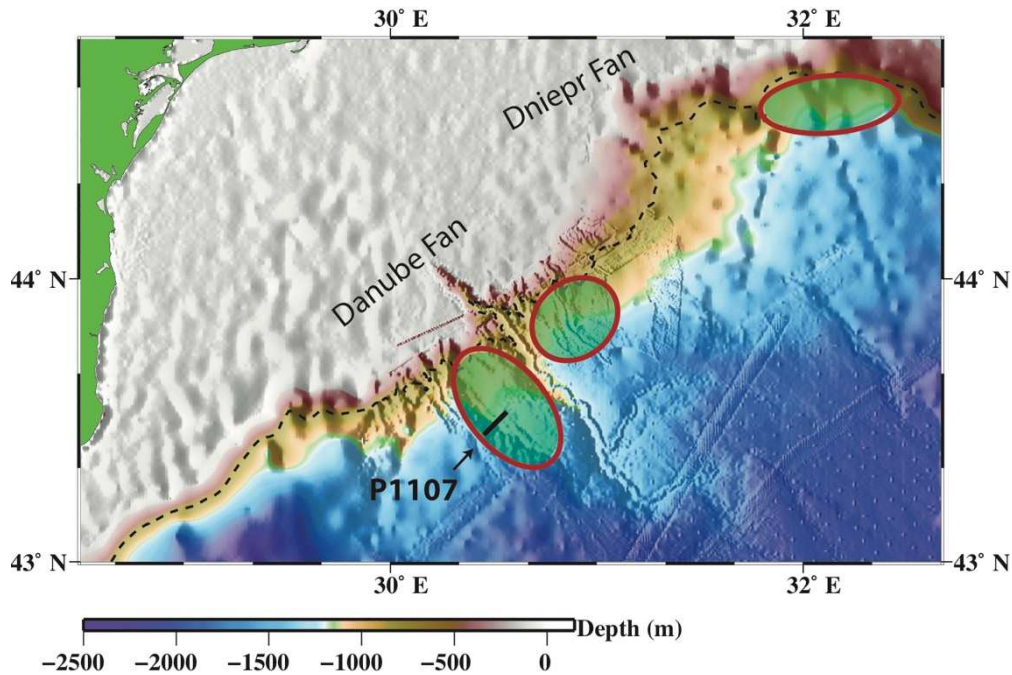
1125

1126 Hydrate was first discovered in the area in a core sample by Yefremova and Zhizchenko (1974), with
1127 the first hydrate sample in the Romanian sector recovered in 2017 (Riboulot et al., 2018). The
1128 existence of hydrate at depth was inferred from BSRs. However their distribution is not continuous
1129 and is limited to a few areas (e.g., Popescu et al., 2007; Zander et al., 2017). Hydrate there is of
1130 microbial origin, with methane $\delta^{13}\text{C}$ values of -84‰ to -70‰ and concentrations of 99.1–99.9%
1131 (Haeckel et al., 2017). Organic-rich Maykopian sedimentary deposits are not in a productive state yet
1132 and do not provide an observable thermogenic methane component.

1133

1134 The HSZ in the northwestern Black Sea is coincident with the Danube and Dniepr fans. Hydrate
1135 formation in the levees or channel base of these fans is inferred from the presence of BSRs, for
1136 example in the Danube fan, where multiple BSRs have been observed beneath ancient levee systems

1137 (e.g., Popescu et al., 2007; Zander et al., 2017; Fig. 18). Zander et al. (2017) inferred that these
 1138 multiple BSRs do not reflect gas composition changes or overpressured compartments, but rather past
 1139 pressure and temperature conditions. Results from thermal models suggest that temperature changes
 1140 related to rapid sediment deposition, rather than bottom-water temperature or sea level variations,
 1141 have a primary influence over the pressure and temperature conditions resulting in the formation of
 1142 multiple BSRs (Zander et al. 2017).

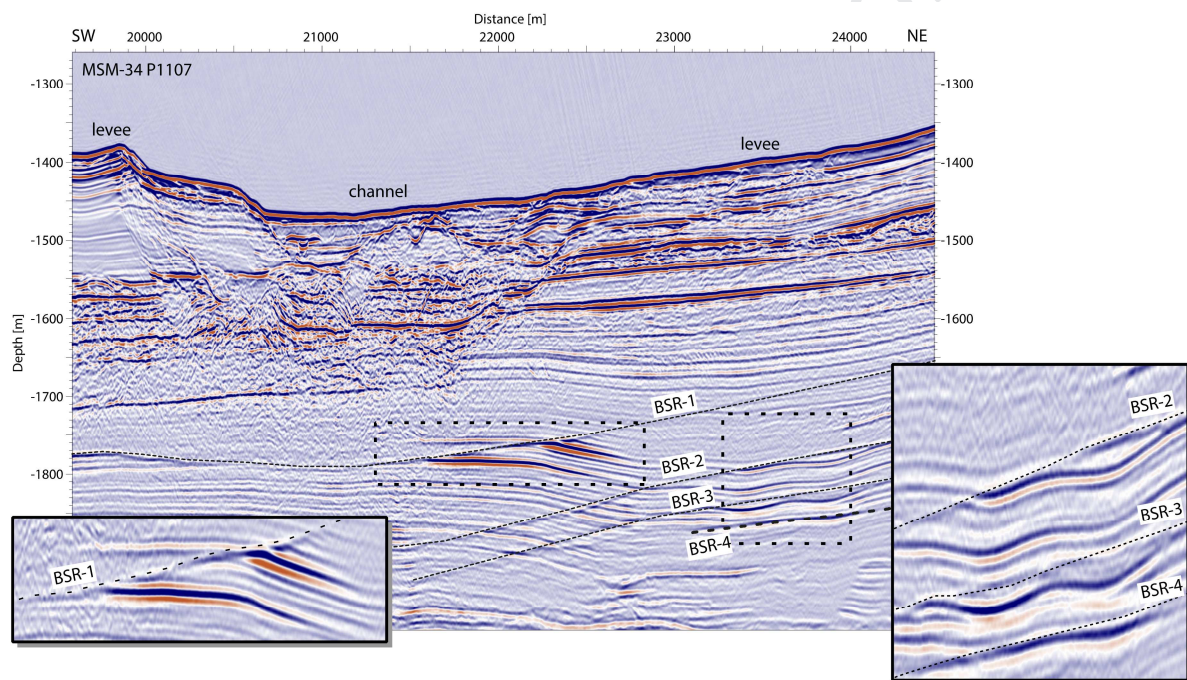


1143
 1144 Figure 17: Bathymetric map of the northwest Black Sea. Background shaded bathymetry from Smith
 1145 and Sandwell (1997) is overlain with shipboard bathymetry compiled by MARUM and GEOMAR.
 1146 Areas with reported gas hydrate indications are marked with shade ellipses. Dashed contour marks the
 1147 upper depth limit of the HSZ at 650 m water depth. Hydrate distribution is derived from Zillmer et al.
 1148 (2005), Popescu et al. (2006), Zander et al. (2017) and Hillman et al. (2018a).
 1149

1150 CSEM data collected across and within the channel levee system shown in Fig. 18 revealed highly
 1151 anomalous resistivity values at various depths within the HSZ, which are partly attributed to lower
 1152 pore water salinities (around 4 ppm; Bohrmann et al., 2018), but also suggest a high hydrate
 1153 saturation of possibly up to 20-30% within the channel filling sediments and below the western levee.
 1154

1155 The availability of structural and stratigraphic constraints from deep-penetrating seismic data has
 1156 enabled the development of a basin scale numerical model to investigate the production and migration
 1157 of gas and resulting hydrate distribution (Hillman et al., 2018a). Sediment structure, slope failures and
 1158 distribution of BSRs are imaged on shallow seismic data (Hillman et al., 2018b; Popescu et al., 2007;
 1159 Zander et al., 2017). These data have enabled the development of a stratigraphy for the slope deposits
 1160 and mass transport events inferred from that of Winguth et al. (2000), although in the absence of
 1161 sufficient sediment samples there remains some uncertainty in the dating of these deposits. Dating has
 1162 come from the ASSEMBLAGE project (Lericolais et al., 2013) and DSDP Leg 42 (Stoffers et al.,

1163 1978). Mapping of active gas seeps using water column imaging, and gas-related structures in seismic
 1164 profiles, have been used to describe the plumbing system in the canyon and levee systems (Hillman et
 1165 al., 2018b). Many of the active gas seeps correlate with sub-seafloor gas migration structures such as
 1166 chimneys or pipes. There is an apparent correlation between gas vents and submarine landslide
 1167 features, but there are insufficient data to determine whether gas migration has played a causative role
 1168 in triggering such slope failure events (Hillman et al., 2018b). Changes in climate, resulting in
 1169 changes in the HSZ, and the identification of paleo seafloors, have together been used to explain the
 1170 origin of the multiple BSRs (Zander et al., 2017). Modelling of the HSZ using inputs from 2D and 3D
 1171 seismic data has indicated that the hydrate system may be in a transient state, with factors such as
 1172 topographic focusing of heat flow playing a significant role in controlling the location and distribution
 1173 of hydrate (Hillman et al., 2018a).

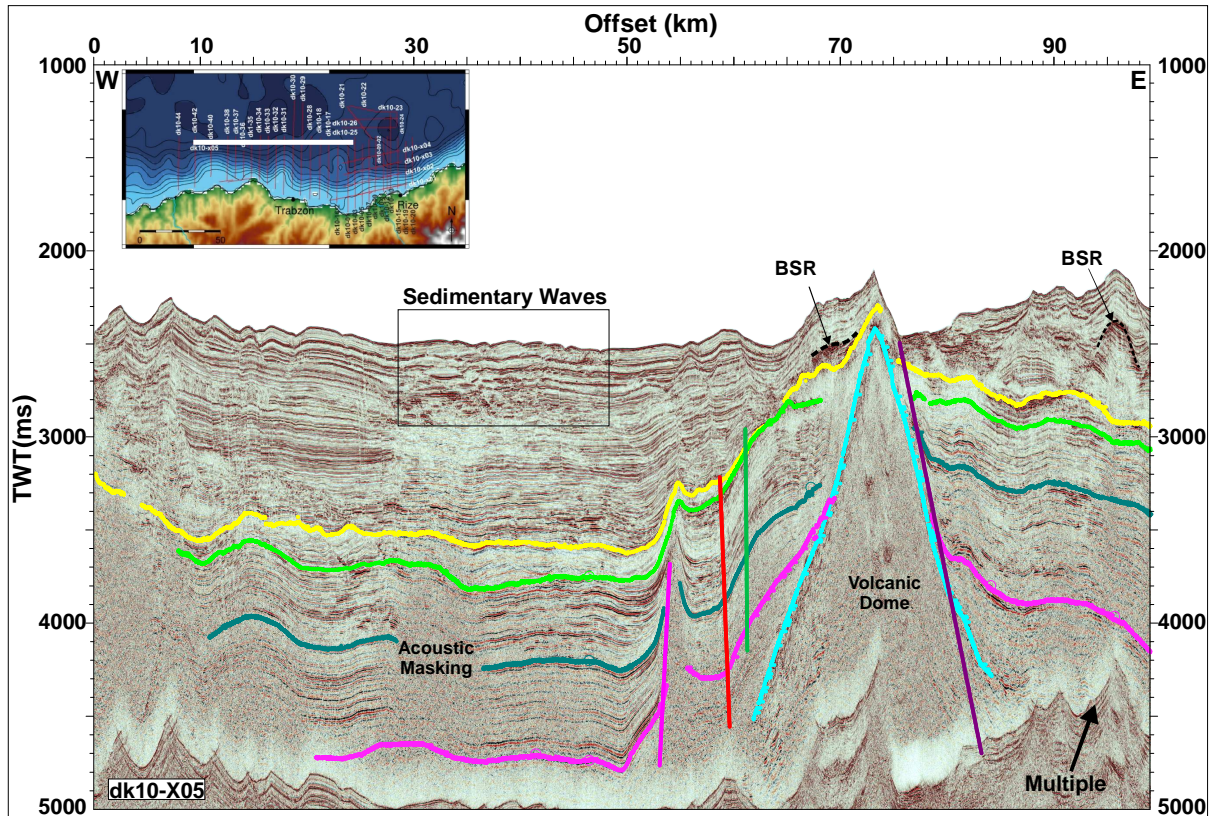


1174
 1175 Figure 18: Multichannel seismic data example of today's BSR (BSR 1) and multiple BSR occurrences
 1176 (BSR 2 to 4) in the Danube fan. While BSR 1 extends over the entire channel levee system the
 1177 multiple BSRs disappear towards the channel structure (SUGAR channel). Insets zoom into the BSR
 1178 events and highlight the increased reflection amplitudes where inversion point and termination
 1179 indicate the BSR position. Data acquired during cruise MSM34 (Bialas et al., 2014).

1180

1181 Seismic velocities from analysis of OBS data were used to provide the first estimates of possible gas
 1182 and hydrate concentrations in the Bulgarian sector of the northwestern Black Sea. The resulting
 1183 velocity-depth sections represent average velocities for sediment packages of about 100 m thickness.
 1184 Estimates of average hydrate saturations in the pore space based on these seismic velocity
 1185 distributions are up to 10% or 30-40%, depending on the hydrate morphology assumed. CSEM data
 1186 were acquired to further investigate gas and hydrate distribution in the sediments. Hydrate saturation
 1187 estimates derived from CSEM datasets depend on the porosity and pore water salinity, and the

1188 appropriate choice of Archie parameters. These studies suggest saturations in the range of 20-30% in
 1189 parts of the HSZ. It is likely that the highest hydrate saturations are located within coarser grained,
 1190 sand-rich sediments in the channel systems and intermittently distributed through the levees (Zander
 1191 et al., 2017).



1192
 1193 Figure 19: Seismic line parallel to coastline offshore Trabzon area, showing fault related volcanic
 1194 dome structure at the eastern side of the section and a BSR at around 300 ms below the seafloor
 1195 (Gunduz, 2015). The Trabzon fault is a strike-slip fault. Acoustic blanking below the BSR may
 1196 indicate free gas. Acoustic blanking is also present in deeper parts of the section.
 1197

1198 11.2.2 Offshore İğneada

1199 Regional seismic data acquired across the continental shelf and slope offshore İğneada (Fig. 16) show
 1200 folded sediments with gas accumulations beneath structural highs, evidenced by seismic blanking
 1201 zones, fluid escape structures and a reef structure (Özel, 2012). Fault systems penetrate the shallow
 1202 sediments beneath these ridges and cross the gas-charged lithologies, suggesting the presence of
 1203 hydrocarbon migration pathways. One profile displays BSRs across the continental slope. However,
 1204 the distribution of hydrate at this site is not well understood due to large inline and cross-line
 1205 intervals. Other profiles show high-amplitude, reversed-polarity reflections that mimic the seabed but
 1206 do not cross-cut stratigraphy, at a depth that is significantly different from that of the unequivocal
 1207 BSRs. The origin of these features remains uncertain. Hydrate was recovered at an acoustically
 1208 transparent feature observed in sub-bottom profiler data that protrudes from beneath the hemipelagic

1209 cover, interpreted as a mud volcano (Fokin et al., 2005). Numerous carbonate-cemented layers and a
1210 mousse-like breccia below were also observed.

1211

1212

Journal Pre-proof

1213 11.2.3 Offshore Zonguldak-Amasra

1214 The Zonguldak-Amasra area is one of the best-studied in terms of shallow gas and hydrate.
1215 Geological and geophysical investigations, including conventional and high-resolution seismic data,
1216 chirp sub-bottom profiler data, multibeam bathymetry and direct sampling, have shown the presence
1217 of gas and indications of gas hydrate (Küçük et al., 2015). Dissolved gas in the shallow sediments
1218 contains hydrocarbons ranging from methane to hexane, suggesting a thermogenic gas source in
1219 addition to microbial gas in the shallow sediments. Seismic evidence for the presence of seven
1220 different mud volcanoes and a large number of buried and active gas chimneys was found in this
1221 region. Widespread seismic blanking zones were observed also beneath the HSZ, with up to 25 km
1222 lateral extent. Chirp sub-bottom profiler data show many chimney structures in the first 40-50 m
1223 below the seabed and sparse gas anomalies were observed on seismic data in various locations. Both
1224 continuous and discontinuous BSRs have been widely observed at this site. Multiple BSRs were also
1225 imaged, with up to five successive BSRs. These additional BSRs may have a similar origin to those
1226 imaged in the Danube fan (section 11.2.1) or may be attributed to a variety of different gas
1227 compositions with different stability limits. In addition to structure I and structure II hydrate, structure
1228 H hydrate might be present at this site, indicated by the presence of i-Pentane gas in a gas
1229 composition similar to that observed in the Gulf of Mexico (Sassen and MacDonald, 1994).

1230

1231 11.3 Hydrate occurrence in the eastern Black Sea

1232 11.3.1 Offshore Samsun

1233 High-resolution seismic data and sediment cores are available from this region (e.g., Dondurur and
1234 Çifçi, 2009). Indications of shallow gas, such as buried and active pockmarks and seismic blanking
1235 zones, were imaged in seismic data. Here, hydrate may be present at relatively shallow water depth
1236 (250-700 m). Bright reflections on the upper slope have been interpreted as hydrate-bearing
1237 sedimentary units. The presence of hydrate at such shallow water depths could be explained by the
1238 presence of hydrogen sulphide in the gas, which shifts the phase boundary to higher temperatures and
1239 lower pressures (Dondurur and Çifçi, 2009).

1240

1241 11.3.2 Offshore Hopa-Rize-Trabzon-Giresun

1242 Three-dimensional seismic data offshore Hopa show the presence of a widespread BSR that is most
1243 prominent beneath structural highs (Minshull and Keddie, 2010). A dense grid of seismic data
1244 offshore Rize and Trabzon showed widespread indications of shallow gas and gas hydrate (Fig. 19).
1245 Chimneys, seismic blanking zones, gas charged sediments, mud diapirs and mud volcanoes are all
1246 present. These were observed around crustal-scale faults that suggest migration from depth. Both
1247 continuous and discontinuous BSRs have been clearly imaged. No hydrate indicators have been
1248 identified in regional seismic data offshore Giresun.

1249

1250 **12. Discussion**

1251 Although methane hydrate is stable in large areas of European margins, numerical models of
1252 microbial gas generation suggest that significant microbial hydrate accumulations are unlikely to be
1253 widespread (e.g., Archer et al., 2009; Wallmann et al., 2012). This result is a consequence of low
1254 predicted organic carbon accumulation rates in the parts of European margins that are deep enough
1255 for hydrate stability. This prediction is supported by observations of particulate organic carbon
1256 concentrations in surface sediments (Wallmann et al., 2012). Consistent with these modelling
1257 considerations, most of the hydrate occurrences described above are associated with conventional
1258 hydrocarbon provinces, and where there are data available on hydrate-forming gas compositions or
1259 isotopic ratios, these data commonly suggest the presence of gas that is at least partly of thermogenic
1260 origin. Direct sampling of hydrate is mostly at fluid escape features such as pockmarks or mud
1261 volcanoes, so we cannot rule out the possibility that the sample locations are unrepresentative.

1262

1263 Offshore Greenland, the search for hydrate is still at an early stage, although the physical and
1264 oceanographic settings of these margins are perfect for hydrate formation. Investigations suggest a
1265 high potential for oil and gas within out- or shallow sub-cropping sedimentary basins in the west and
1266 northeast Greenland margins. The onshore observations of oil seeps in central west Greenland
1267 confirm the existence of an active hydrocarbon system here and the discovery of onshore hydrate
1268 indicates that gas is migrating from the system and likely forms hydrate. Such gas migration is also
1269 suggested by indirect evidence from seismic and shallow cores offshore. Further offshore on the west
1270 Greenland margin, observed BSRs and seismic blanking may also provide evidence of hydrate
1271 occurrence. Thus it is likely that hydrate is present on the central west Greenland margin and, based
1272 on the onshore oil discoveries, the hydrate could contain a high portion of thermogenic gas. Hydrate
1273 has not yet been reported on the east Greenland margin, which is likely due to the lack of research and
1274 wells on this margin. However, a gas-show in ODP well 909, together with the presence of BSRs and
1275 other seismic indicators, may provide evidence for an active hydrocarbon system forming hydrate in
1276 the northeast Greenland margin.

1277

1278 Offshore Svalbard, the hydrate system has characteristics that may be unique among hydrate systems
1279 worldwide. It stretches from the continental slope onto the mid-ocean ridge, thereby experiencing
1280 significant changes in thermodynamic conditions, and it may be the only hydrate system in the world
1281 that forms from hydrocarbon gas of three different sources, namely microbial, thermogenic and
1282 abiotic gas. However, the relative contribution of each of these sources is still unknown and may
1283 show significant local variations. The structural-stratigraphic development of this area has led to the
1284 formation of distinct sedimentary depocentres and fluid migration pathways, thereby controlling the
1285 distribution of hydrate. At present, the total distribution extends over approximately 4000 km² with

1286 the main accumulation in the Vestnesa Ridge and many smaller patches of hydrate in close vicinity.
1287 Yet large parts of this area remain unmapped and potentially hold much more hydrate if the
1288 hypothesized abiotic origin of gas in hydrate is confirmed as a potential hydrate play. Nonetheless,
1289 current estimates of hydrate saturations so far are sufficiently low that the economic value of hydrate
1290 offshore Svalbard is questionable.

1291

1292 Onshore Svalbard, on average, the modelled HSZ thickness reaches 300 m, with the thickest zones
1293 extending from about 75 m to up to 725 m below the surface, which are the minimum and maximum
1294 depths at which hydrate is expected to form, based on regionally constrained thermobaric conditions.
1295 Variable pore water salinities, anomalous regional pressure regimes, uncertainties in regional
1296 geothermal gradients and changing temperature conditions put a limit on the model's accuracy further
1297 away from Nordenskiöldland, where regional datasets and constraints afford good control. In
1298 addition, the model takes no account of factors likely to control hydrate presence, such as fluid
1299 migration pathways and local biogeochemistry. The ongoing study of the onshore HSZ in central
1300 Spitsbergen and archipelago-wide is pivotal to the mapping of the potential occurrence of onshore
1301 hydrate accumulations and compliments the significant findings made offshore.

1302

1303 The Barents Sea exhibits widespread evidence for thermogenic hydrate occurrence and is a unique
1304 region where hydrate is hosted in consolidated sedimentary formations and likely co-exists with
1305 conventional petroleum reservoirs. Seismic data analysis by Laberg et al. (1998) and patchy BSR
1306 distribution indicate relatively low resource potential, but the free gas trapped beneath the BSR could
1307 still be of commercial interest. Despite increased petroleum exploration activities in recent years,
1308 none of the BSRs identified in the southwest Barents Sea have yet been drilled or sampled. The
1309 presence of hydrate stability conditions within the major shallow reservoirs in the region, however,
1310 has attracted increased attention towards hydrate from commercial exploration companies (Norwegian
1311 Petroleum Directorate, 2018).

1312

1313 On the mid-Norwegian Margin, the BSR only occurs within finely bedded contouritic and
1314 hemipelagic deposits (mainly silty clays) of the Quaternary Naust formation, which seem to be the
1315 favourable host sediments for hydrate. The extent of hydrate is geologically controlled by hydrate
1316 stability conditions that exclude hydrate on the continental shelf, and the availability of the suitable
1317 host rock elsewhere. Bünz et al. (2003) suggest that hydrate on the mid-Norwegian margin develops
1318 from fluids that originate far beneath the HSZ. Deep-seated Cenozoic dome structures with inferred
1319 hydrocarbon reservoirs might be one source of gas, though gas compositions from limited sampling
1320 suggest a primarily microbial origin. Using the approach of Max and Johnson (2016), hydrate on the
1321 mid-Norwegian margin can be classified as a low grade deposit with little economic value.

1322

1323 Offshore Ireland, the Druid Anomaly over the Feni Drift in the Rockall Basin, and contourite deposits
1324 in the Porcupine Basin, have been identified as potential targets for further hydrate exploration.
1325 Furthermore, exploration in deep water for conventional hydrocarbons in the South Porcupine Basin
1326 requires better definition of the HSZ to mitigate against the risk of hydrate dissociation while drilling
1327 and consequent uncontrolled gas release. More seismic interpretation, followed by seabed sampling
1328 and shallow drilling, are required to identify hydrate. As more conventional oil and gas wells are
1329 drilled offshore Ireland, new geothermal gradient data will be acquired that will contribute to a better
1330 definition of the HSZ.

1331

1332 On the northwest continental margin of Iberia, the occurrence of hydrate is uncertain. Although some
1333 data suggest that the sedimentary and geomorphological evolution of the area is controlled by fluid
1334 dynamics associated with gas seepage, and occasional weak indicators of gas have been described
1335 (e.g., possible BSR, seismic bright spots and liquefaction of a sediment core), none are conclusive.

1336

1337 On the South Iberia and Northwest Africa margins, direct evidence for hydrate has been found only in
1338 the mud volcanoes of the Gulf of Cádiz. Indirect evidence has been detected on both sides of the
1339 Straits of Gibraltar, mostly associated with mud volcanoes and mud diapirs, but also in the form of
1340 localised BSRs, degassing and liquefied sediments in cores, and by the presence of chlorinity
1341 anomalies. The preferred migration pathways for fluids into the basin are the main tectonic structures
1342 such as diapirs, folds and faults. The composition of the pore fluids and hydrate sampled in the Gulf
1343 of Cádiz indicate generally a mixture of microbial and thermogenic sources. However, in some mud
1344 volcanoes associated with the deep SWIM strike-slip faults, an abiotic source is also possible,
1345 connected to hydrothermal fluids in the oceanic domain. Thus the Gulf of Cádiz has a variety of
1346 sources of gas and geological settings for hydrate formation. In the case of the Alborán Sea, gas is
1347 present in diapiric formations originating in the basal allochthonous unit and is likely to be
1348 thermogenic.

1349

1350 In the Eastern Mediterranean, hydrate sampling is also limited to mud volcanoes. There is little
1351 published work on seismic indicators of hydrate presence, although extensive exploration datasets
1352 provide opportunities for further analysis. The high sensitivity of the ocean here to climate and
1353 oceanographic changes may provide a natural laboratory to investigate the influence of these changes
1354 on hydrate stability, as well as the potential impacts.

1355

1356 In the Sea of Marmara, there is abundant evidence for the presence of gas within the HSZ and hydrate
1357 has been directly sampled in the top of a mud volcano, but unequivocal BSRs have not been observed,
1358 so the amount of the hydrate present is difficult to assess.

1359

1360 In the Black Sea offshore Romania and Bulgaria, diverging results on possible hydrate saturations
1361 demonstrate the need to ground-truth models by collecting samples from deep drilling with logging
1362 and core sampling. Physical sediment parameters, heat-flow measurements, geochemical data and
1363 sediment dating are required to calibrate the remote sensing techniques and to enable the extension of
1364 available models along the margin. Changes in climate such as the last glacial maxima (LGM) caused
1365 a bottom water temperature decrease from 9° C to about 4-6° C, a sea-level decrease of about 120 m
1366 and the development of limnic conditions as the Bosphorus interface to the Mediterranean was closed.
1367 These changes caused a decrease in the maximum thickness of the hydrate stability field by about
1368 33%, from 550 m to 370 m (Zander et al. 2017). This change may have released 1.1-4.6 Gt of
1369 methane carbon as the hydrate dissociated (Poort et al. 2005). Ongoing salinity increases in the Black
1370 Sea sediments will shift the top of the HSZ in the future, causing further hydrate dissociation
1371 (Riboulot et al., 2018). Furthermore, a mis-match between modeled HSZ limits and observed BSR
1372 depths suggests that the hydrate system of the Black Sea is currently not in equilibrium but is
1373 approaching steady state (Hillman et al., 2018a).

1374
1375 On the southern continental slope and rise of Black Sea, BSR occurrences are mapped in water depths
1376 of 750-2000 meters from high resolution multichannel seismic reflection data. Also, chirp data suggest
1377 the presence of gas accumulations at shallow sediment depths (30-40 m). Slope failures are widespread
1378 along both the western and eastern steep canyon systems. The presence of hydrate is not restricted to
1379 these areas but is probably much more extensive. Hydrate samples have been reported widely across the
1380 Turkish Black Sea margin in BSR and mud volcano areas. Free gas is inferred to occur beneath the
1381 BSR, as indicated by seismic bright spots and areas of seismic blanking. The presence of gas seeps to
1382 the seabed through the hydrate stability zone, via mud volcanoes and fault zones, provides evidence for
1383 free gas below the hydrate zone. Mapping of active gas seeps using water column imaging and sampling
1384 of free gas in water samples and sediments will give information about the origin of the gas, which
1385 could be microbial or thermogenic or both, as in the Amasra area.

1386

1387 Thus we can categorise areas covered by our study into three types:

- 1388 1. Areas of widespread BSRs: the Davis Strait, Fram Strait, the mid-Norwegian margin, and the
1389 southern margin of Black Sea.
- 1390 2. Areas where there is no BSR, or the BSR is localised rather than widespread, but hydrate has
1391 been directly sampled: the Barents Sea, the Gulf of Cadiz, the Eastern Mediterranean, the Sea of
1392 Marmara, and the Black Sea offshore Bulgaria and Romania.
- 1393 3. Areas with neither a clearly identified BSR nor direct sampling of hydrate, but where other
1394 more indirect hydrate indicators are present: the Disko area offshore west Greenland, the
1395 northeast Greenland margin, onshore Svalbard, offshore Ireland, and offshore northwest Iberia.

1396 Where hydrate has been sampled, it usually contains higher hydrocarbons, indicating a thermogenic
1397 component; an exception is the Black Sea offshore Romania and Bulgaria, where only trace amounts of
1398 higher hydrocarbons are present.

1399

1400 **13. Conclusions**

1401 From our review of hydrate occurrence around Europe, we conclude:

- 1402 1. There is direct or indirect evidence for the presence of hydrate in several European locations
1403 including the western and eastern margins of Greenland, onshore and offshore Svalbard, the
1404 Barents Sea, the mid-Norwegian margin, the Atlantic margin of Ireland, the eastern
1405 Mediterranean Sea, the Sea of Marmara, and the western and southern margins of the Black
1406 Sea.
- 1407 2. Hydrate is observed to be particularly widespread offshore Svalbard and Norway and in the
1408 Black Sea.
- 1409 3. Areas with strong evidence for the presence of hydrate commonly coincide with conventional
1410 thermogenic hydrocarbon provinces.
- 1411 4. Although hydrate systems are well explored in a few small areas, for most European margins,
1412 significant further research is needed to determine the regional abundance of hydrate beneath
1413 the seabed.

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Journal Pre-proof

There is direct and indirect evidence for hydrate occurrence in several areas around Europe

Hydrate is particularly widespread offshore Norway and Svalbard and in the Black Sea

Hydrate occurrence often coincides with conventional thermogenic hydrocarbon provinces

The regional abundance of hydrate in Europe is poorly known

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