# **Environmental challenges related to methane hydrate decomposition from climate change scenario and anthropic activities: State of the art, potential consequences and monitoring solutions**

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#### **Abstract :**

Natural gas hydrate deposits (NGHD) have been investigated for decades and represent one of the major methane reservoirs on Earth. They are encountered in sediment of both the continental margins and the permafrost region; areas considered to host amongst the most climate-sensitive ecosystems on Earth. With worldwide temperature increases affecting continental margins and the permafrost, it is important to raise concern about the fate of the NGHD in the coming centuries. Thus, this review presents an overview of the potential consequences of hydrate decomposition on its surrounding areas. It compiles and discusses hydrate-derived methane fluxes measured or inferred from in situ data at several sites by considering both dissociation and dissolution. Depending on the magnitude and the duration of hydrate decomposition, the amounts of methane released can affect to varying degrees the seafloor and the microbial communities that sustain the methane cycle and regulate its transfer from the sediment to the water column; and that aspect is addressed in this review. Here, we also considered the transfer of methane from NGHDs and more broadly from marine emissions to the atmosphere, as it is assumed that such transfer will likely increase in the future. Finally, multi-scale monitoring in space and time is a key element to evaluate the impacts of natural and anthropic perturbations on NGHDs. We thus propose potential engineering solutions for the monitoring of NGHD, mainly based on the long-term deployment of sensor systems.

**Keywords** : Continental margins, gas emissions, methane flux into the atmosphere, natural gas hydrate deposits, permafrost and slope stability

### **1. Introduction**

Natural gas hydrate deposits (NGHD), one of the major methane  $(CH_4)$ reservoirs on Earth, are mainly located on continental margins, generally at water depth beyond ~500 m (Max, 2003; Max and Lowrie, 1996; Mienert et al., 2022; Milkov, 2004; Paull and Dillon, 2001; Ruppel, 2011). They are found in the upper sedimentary interval where the temperature is rather low (below 4 °C at the sediment-water interface for open seas) to meet their stability requirements. On continental margins, NGHD are generally encountered within the sediment at cold seep areas, which are specific ecosystem areas characterized by natural gas emissions at the seafloor (Sassen et al., 1993; Suess, 2014; Villar-Muñoz et al., 2021). Outcropping hydrates are less common but can also be observed at sites characterized by intense  $g_{\alpha}$ , enting (MacDonald et al., 1994; Olu et al., 2009; Sassen et al., 1999). The amount  $c<sup>f</sup>$  rule rethane stored within the marine hydrate-bearing sediments ranges between 3-1469 GtC (Burwicz et al., 2011; Lee et al., 2022; Pinero et al., 2013; Wallmann et al., 2012). Methane released from hydrates promotes the development of chemos nthetic communities. At the higher latitude, in Polar Regions where the temperature is a most permanently below freezing point, natural gas hydrates are found in the permafrost at shallower water depth. The mind map in Figure 1 illustrates the large variety of disciplines the studies of the dynamics of NGHDs can collate: from field work including observations, sampling and monitoring, to laboratory study with an. tyses, modeling and forecast. Such studies are also relevant for societal issues such as civil protection and offshore industrial safety when dealing with seafloor stability,  $\sigma$  as emissions, climate change adaptation, meeting energy needs, and preservation of chemosynthetic ecosystems. Tackling these issues 1993; Suess, 2014; Villar-Muñoz et al., 2021). Outcropping 'nydra<br>but can also be observed at sites characterized by intense  $g^r_{\text{so}}$  "en.in<br>1994; Olu et al., 2009; Sassen et al., 1999). The amount  $\sqrt{r}$  r.ietha<br>mari



Figure 1: Mind-map representing the principal hydrate-driven scientific researches with the societal issues.

The hydrate-bound gases either come from  $\alpha$ , is thermogenic reservoirs that contain methane, and usually a significant amount of  $h^{\alpha}$  ier hydrocarbons (often called  $C_{2+}$ ), or are generated by the microbial degrad  $\mu$  in  $\sigma$ . organic matter at shallower sedimentary depth, that produces mainly methane (Kvenvolden, 1995; Milkov, 2005; Milkov and Etiope, 2018; Whiticar, 1994, 1992). The presence of hydrocarbons other than methane in the hydrate-bound gases expands the hydrate stability field towards lower pressure and higher temperature. For instance, thermogenic hydrates are found in the Sea of Marmara at ~660 m water depth and ~15 °C (Bourry et al., 2009), whereas the microbial gas hydrate depositions of the Romanian sector of the Black Sea is located at >700 m water depth and  $\degree$  °C (Burwicz and Haeckel, 2020; Chazallon et al., 2020; Ker et al., 2019; Riboulot et al., 2018; Zander et al., 2017). Civil<br>
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Most of the NGHD in ventoried on Earth contain microbial gases. Thus, they are more sensitive to changes in temperature, pressure and fluid chemistry, especially salinity. Any changes in one of these physicochemical parameters can trigger their decomposition (also called breakdown), leading to the discharge of the hydrate-bound gases into the water column, with potential input into the atmosphere (Schmale et al., 2005; Shakhova et al., 2010; Solomon et al., 2009; Thatcher et al., 2013; Westbrook et al., 2009). Here, the term decomposition refers to either dissolution with release of methane-enriched water, or dissociation when the NGHD is brought outside its stability field and the hydrates are fully decomposed into water and free gases. Previous studies have shown that other natural geological processes such as tides, seismic activity, seawater infiltration, change in the Gulf Stream current, or the decrease and cease in gas supply may also trigger hydrate decomposition (Lapham et al., 2013; Phrampus and Hornbach, 2012; Riboulot et al., 2018; Sultan et al., 2014). Less frequently observed in nature, hydrate-piece detachment has been proposed as a possible mechanism for

causing the degradation of NGHD and allowing the transfer of significant amounts of methane into the hydrosphere (Pape et al., 2011a).

Furthermore, hydrate decomposition changes the mechanical properties of the subsoil and affects the seafloor stability (Fig. 1). Such decomposition can enhance the formation of seafloor structures like pockmarks and carbonate build-up, and/or can also trigger sediment sliding (Hovland et al., 2002; Maslin et al., 2010; McConnell et al., 2012; Sultan et al., 2014; Yan et al., 2020). Climate change and/or anthropogenic activities are amongst the two major processes that may cause NGHD decomposition in the future (Dickens, 2001; Dickens and Quinby-Hunt, 1997; Kennett et al., 2003; Marcelle-De Silva and Dawe, 2011; Moridis and Collett, 2003; Moridis et al., 2009; Ruppel, 2011; Ruppel and Kessler, 2017; Schicks et al., 2011; Vargas-Cordero et al., 2020b). Seabed deformation and prolonged release of methane in the water column are the two main hazards related to hydrate decomposition (Mas.in et al., 2010), and they may have severe consequences on the dynamics of the surrounding ecosystems (Fig. 1). Thus, NGHD decomposition may be considered as a  $t_1$  reat to the biodiversity of these ecosystems. However, they also represent a potential energy resource (Fig. 1) and several countries have undertaken comprehensive programmes for hydrate inventory on continental margins located within their Exclusiv  $\angle$  Economic Zone (EEZ), with the aim of estimating the amount of methane that can  $b\text{/}1$  scovered (Boswell et al., 2017; Collett et al., 2014; Collett et al., 2012; Konno et al., 2017; Li et al., 2018; Ruppel et al., 2008). It is worth noticing that current solutions for methane production from NGHD are not economically viable, and our increasing awareness of climate change requires us to advance our researches on the understanding of natural-gas hydrate dynamics and its relevance in the global carbon  $c_1$ . Such research studies are key to developing sustainable solutions for the aforementioned societal issues. deformation and prolonged release of metha.  $\bullet$  in t<br>addition and prolonged release of metha.  $\bullet$  in t<br>azards related to hydrate decomposition (*l* ias.<sup>1</sup>n et<br>exonsequences on the dynamics of the surrounding<br>ecompositi

Furthermore, it is worth  $em_{\nu}$  hasizing that the time scale of hydrate decomposition can extend from a few years to nillennia, depending on the nature of the disturbance. Thus, here we define disturbances leading to short-term decomposition as resulting from processes that significantly affect the NGHD after few years from their onset; whereas disturbances leading  $\rightarrow$  long-term decomposition refer to processes for which the impacts on the NGHD appear after few decades, centuries or millennia. For instance, the influence of temperature change on hydrate stability is different when considering hydrate production (short-term human-induced disturbances to recover the methane as quick as possible) and climate change (long-term human-induced disturbances). Indeed, as an example of disturbance leading to long-term decomposition, modeling of the West Svalbard by Thatcher et al. (2013) and Marín-Moreno et al. (2015), respectively, suggested that the delay between the onset of warming and the inception of gas emissions due to this warming could amount to  $\sim$ 20-30 years. Such a time lag is not conceivable for hydrate production induced by thermal stimulation for instance. The magnitude of the decomposition and its duration also raise the question of the resilience and adaptation of the ecosystems associated with these deposits.

In this paper, an analysis of the environmental challenges associated with the decomposition of NGHD is proposed. It starts with a detailed description of the possible hazards related to the decomposition of NGHD and their consequences on the marine ecosystems considering disturbances leading to both short-term and long-term decomposition. Finally, it discusses possible monitoring solutions to assess the state of decomposition of a deposit and quantify the gas discharge over time.

### 2. **Prerequisites and main factors governing hydrate dynamics**

The necessary thermodynamic conditions to form and sustain hydrate growth within sediments are the saturation of pore water with gas in coexistence or not with free gas, low temperature and high pressure. A failure of one of these three prerequisites will systematically trigger hydrate decomposition. However, several other factors govern the formation, distribution and extent of gas hydration nature. Amongst them, the physicochemical properties of the hydrate-forming geometries and the sediment  $(e.g.,)$ gas generation and transport processes, gas fluxes, pore-water salinity, sediment mineralogy and permeability) and the geologic<sup> $\ell$ </sup> characteristics of the setting (*e.g.*) tectonics and fluid transport pathway, sedimentation regime and lithology, geothermal gradient and heat flux pattern) are key poin's. These factors affect both the formation and the decomposition of hydrates to var  $\sin \theta$  extents as stressed in previous review papers (Hassanpouryouzband et al., 2021; Malagar et al., 2019; Ruppel and Waite, 2020; Waite et al., 2009), making the  $p_1$ , diction of the consequences of changing any of them on the surrounding geosphere as well as on the hydrosphere, and potentially the atmosphere, a challenging task.  $S_u$  a prediction becomes even more demanding once we consider that the accumulation  $\mathcal{F}$  natural gas hydrates within the sediments is a time and space-evolving process  $\alpha$  to the continuous changes in the deposit permeability and thermal properties that, in turn, continuously modifies the hydrate growth kinetics, the gas flow regime and pathway, and thus reroutes their distribution pattern (Schmidt et al., 2022). Such a *b*ehavior explains the wide varieties of hydrate habits encountered in nature, from disseminated through lens to massive nodules, and its heterogeneous distribution within the ediment from microscale to kilometer scales (Daigle and Dugan, 2011a, b; Egeberg and Dickens, 1999; Guo et al., 2020; Kossel et al., 2018; Naudts et al., 2012; Pape et al., 2011b; Paull and Dillon, 2001; Simonetti et al., 2013; Solomon et al., 2014; Stern and Lorenson, 2014; Stern et al., 2011; Wang et al., 2020). Thus, the knowledge of how all the aforementioned properties and factors affect the hydrate dynamics is often site-specific and depends on the geological history of the setting. Nevertheless, these properties are critical to predicting and quantifying the macroscale responses of hydrate-bearing sediments to environmental changes at different time scales. The environmental challenges are primarily related to gas hydrate decomposition, which also leads to severe and time-evolving changes in the permeability field of the deposit. The magnitude of the decomposition and how it happens strongly depend on the nature and magnitude of the disturbances applied to the NGHD. The following section focuses on the environmental challenges related to mperature and high pressure. A failure of one of the<br>ally trigger hydrate decomposition. Hov  $\epsilon, \gamma$ , sation, distribution and extent of gas hydrates in na<br>aical properties of the hydrate-forming geo luids a<br>and transport

anthropic (human-induced) disturbances and climate change. As explained above, the first corresponds to short-term perturbations with localized consequences, while the second induces disturbances spanning over a larger timescale and with broader impacts.

## **3. Environmental challenges related to hydrate decomposition**

## **i. Impact of hydrate decomposition on the seafloor morphology and stability**

Methane hydrate formation and decomposition induce the build-up or loss of solid materials that have a density significantly different from that of pore water or free gas (Lee et al., 2010; Loreto et al., 2011; Pape et al., 2011a). Density difference is one of the physical mechanisms that drives seafloor deformation. Several studies have demonstrated that hydrate formation and decomposition modifies the regime and pathway of free gas migration through the sediments, and can strongly affect the morphology of the seafloor by creating or enhancing the formation of pockmarks, mounds or pingos (Andreassen et al., 2017; de Prunelé, 2015; Gupta et al., 2022; Hovland and Svensen, 2006; Loreto et al., 2011; Paull et al., 2007; Riboulot et al., 2016; Serié et al., 2012; Sultan et al., 2014; Sultan et al., 2010; Taleb et al., 2020; Vargas-Cordero et al., 2020a; Waage et al.,  $2\sqrt{2}$ ;  $\angle$  ander et al., 2020). Besides the formation and decomposition of hydrates, dislodgement of hydrate pieces has been proposed to explain the rough seafloor topography encountered in the Eastern Black Sea (Pape et al., 2011a). While the hydrate formation stores methane within the sediment, the melting of hydrates triggers its release, and this is accompanied by the development of excess pore pressure that, in turn, reduces the mechanical strength of the sediment (Le et al., 2020; Nguyen-Sy et al., 2019; Sultan et al., 2007). In the rest of this section, we will focus on the consequences of hydra $\mu$  decomposition as this process can trigger sediment mass flow (Sultan et al.,  $2004$ ), which can be prodigious in scale and generate damaging tsunamis on open continental slopes (Talling et al., 2014). ave a density significantly different from the it of perceptions.<br>
Thereto et al., 2011; Pape et al., 2011a). Density diventising that drives seafloor deformation. See and hydrate formation and decompositio, modifie gas m

In nature, hydrate dissolution is more widespread than dissociation because dissolution does not require the significant amount of energy needed to take the system outside its stability field (Ruppel and Waite, 2020). It can result from the shutdown or the slowdown of the gas flux supplying the NGHD, or an increase in either the pore water salinity or the bottom water temperature. Very few works mention explicitly the consequences of hydrate dissolution on the seafloor. Sultan et al (2010, 2014) showed that the formation of pockmarks in the Nigeria deep-water and the evolution of their morphology are strongly related to hydrate formation and dissolution. The observed pockmarks can be 40 m depth and nearly a kilometer in diameter, making the installation of offshore oil and gas production facilities in their close vicinity a risky task. The dissociation of natural hydrates requires severe and more rapid changes in the (T, p) conditions. It can result from an increase in the bottom water temperature or a decrease in the hydrostatic pressure (Andreassen et al., 2017; Marin-Moreno et al.,

2015). Most of the existing articles on the impact of gas hydrate decomposition on the seafloor mentioned hydrate dissociation explicitly.

The role of gas hydrate dissociation on submarine slope instability has been investigated over decades but controversy persists (Collett et al., 2014; Hassanpouryouzband et al., 2020). Dillon and Max (2000) have argued that dissociation of gas hydrates can be considered as the main cause of submarine slope failure only when the three following criteria are met: (*i*) gas hydrates are widespread; (*ii*) slides are initiated in areas within the hydrate phase boundaries; and (*iii*) sediment of low permeability (mainly finegrained sediments) is present at the base of the gas hydrate occurrence zones. There are two well-studied submarine slope failures that happened in interglacial periods that have been potentially attributed to hydrate dissociation, although debate still remains: Storegga Slide and Hinlopen Slide. The Storegga Slide is one of the largest submarine slope failures known to have happened 8000 years ago (Fugge et al., 1988). The slide was most likely triggered by a strong earthquake and developed as a retrogressive slide, where massive sediments of about 150-200 m thick and  $\mu$  to 10.30 km wide slid down over  $\sim$ 200 km, causing huge tsunamis (Bryn et al.,  $\sim$  0.5). Besides, data presented few years ago (Geissler et al., 2016) strongly indicates that gas hydrates, free gas and excess pore pressure may have been the trigger or  $\mathbb{R}^+$  least supportive factors for the slope instabilities north of Svalbard, in the vicinity of the Hinlopen Slide. Considering other locations, Lee argued that hydrate dissociation might have played a role in the large submarine landslides on the US Atlantic margin (Lee, 2009). Gas hydrate dissociation during deglaciation phases was a'so mentioned as one of the possible climate-driven changes that significantly affected  $\triangle$ lope stability in the Mediterranean Sea (Urgeles and Camerlenghi, 2013). In another recent work, by considering a seafloor temperature increase of 2 or 4  $\degree$ C, Alessandrini et al (2019) simulated the impact of future global warming over the next 50 and 100 years on the Gas Hydrate Stability Zone (GHSZ) off the Chilean margin. They suggested that, despite an increase in hydrostatic pressure due to sea level rise, seaf<sup>1</sup> $\circ$ <sup>1</sup>  $\circ$  temperature increase would induce the dissociation of the entire NGHD located along the upper slope in the next century. The dissociation will cause slope instability in some areas, and could seriously damage coastal cities if this dissociation triggers tsunamis. Using a large geophysical dataset including bathymetry and 2D/3D P-cable seismic data, Hillman et al. (2018) investigated the potential relationship between gas migration pathways, gas vents observed at the seafloor and submarine slope failures near the S2 Canyon in the Danube fan (Northwestern Black Sea). They found abundant evidence for gas migration in the area that suggests a connection between slumps and gas migration, although it is not clear whether gas migration facilitates slope failure through pressure and pre-conditioning of the sediments, or vice versa. From 2D seismic reflection profiles along the active margin of northern Colombia in the western Caribbean Sea, Leslie and Mann defined a series of three giant, previously unidentified, submarine landslides (Leslie and Mann, 2016). They suggested that an over-pressurized zone of weakness located at the boundary of the hydrate stability has likely facilitated slope failure. y attributed to hydrate dissociation, alth vigh d<br>and Hinlopen Slide. The Storegga Slide is one of t<br>nown to have happened 8000 years ago (1 ugg > et<br>triggered by a strong earthquake and d/ver ped as<br>eediments of about 15

Since the early works of McIver (1982), several studies have argued for a causal link between gas hydrate dissociation and the occurrence of submarine landslides (Bünz et al., 2005; Dawson et al., 2011; Elger et al., 2018; Grozic, 2010; McIver, 1982; Mienert et al., 2005). Such a link was supported by theoretical considerations based on the loss of cementation coupled with the release of free gas, giving rise to the development of excess pore pressure when changes in environmental conditions are no longer favorable for stable gas hydrates (Sultan et al., 2004; Tinivella and Giustiniani, 2013). Indeed, the dissociation of hydrates at the basis of their stability field could liberate free gas and increase the pore pressure just beneath the Bottom Simulating Reflector (BSR), and consequently decrease the effective normal stress (Hornbach et al., 2004). Thus, such focused dissociation weakens the strength of sediments due to loss of hydrate cementation between grains (Brown et al., 2006; Tinivella and Giustiniani, 2013). In the last two decades, the role of excess pore pressure (overpressive) on submarine slope instability has been very often put forward. The overpressure could potentially  $(i)$ facilitate or trigger submarine slides, (ii) form nearly vertical columns of focused fluid flow and gas migration, and (iii) determine the failure of  $\alpha$  permeable layer in presence of low-permeability zone (Xu and Germanovich, 2006). Recent analyses aiming to assess quantitatively the role of gas hydrates  $\alpha$  submarine slope instability have highlighted the importance of sediment  $\text{lit}_i$  (Handwerger et al., 2017) and drainage conditions (Priest and Grozic, 2016), or fracture formation (Yang et al., 2018) on the development of excess pore preserved during hydrate dissociation. Mountjoy et al. (2014) analyzed seismic reflection data of the Tuaheni landslide complex (New Zealand East Coast) and proposed that, gas hydrates can directly destabilize the seafloor via three mechanisms (Mountjoy  $\alpha$ <sup>t</sup> al., 2014): (1) excess pore pressure induced by gas hydrate dissociation; (2) hydro-fracturing in the gas hydrate zone; (3) and timedependent plastic deformation of hydrate-bearing sediment. Recently, unlike previous studies, Gross et al.  $(2018)$  performed a 3D analysis of the distribution of gas and gas hydrate indicators and did  $\mathbf{h}$ , show evidence of gas hydrates within the upper landslide unit. However, their observations support the hypotheses of Mountjoy et al. (2014) that argue that build-up of overpressure below low permeability gas hydrate-bearing sediments could cause 'iydro-fracturing in the gas hydrate zone and valving excess pore pressure into the landslide body. The hypotheses also suggested that gas is migrating into the critical mechanical zone at the base of the landslide, and thus building up overpressure that can lead to the reactivation of the landslide. Results obtained by Horozal *et al.* (2017) in the Ulleung Basin also suggested that excess pore pressure caused by gas hydrate dissociation could have contributed to slope failures. Such an increase in the interstitial pore pressure generated by gas hydrate dissociation was equally reported by Ker et al. (2019) in the Western Black Sea. They suggested that values of excess pore pressure of 1-2 MPa are probably the result of the low permeability of hydrate-bearing sediments. This excess pore pressure is expected to drastically reduce sediment stability and could be at the origin of some of the observed landslides in the area. Such assumptions agree with the study of Elger et al. (2018) who used reflection seismic data from the Arctic Ocean and numerical modeling to show a direct link between hydrates and slope instability. Their study showed that hydrates ween grams (Brown et al., 2006; Tinivella a id Gius<br>s, the role of excess pore pressure (overpress. ve)<br>been very often put forward. The overpress. ve)<br>been very often put forward. The overpress ince-<br>ger submarine slides

reduce the sediment permeability and causes the build-up of overpressure at the base of the GHSZ. This overpressure reaches the shallow permeable beds, through hydrofracturing forms like pipe structures, and then it is transferred laterally within the sedimentary column, weakening the slope sediment and leading to its destabilization.

Hovland and Gudmestad discussed the engineering significance of gas hydrates and the possible engineering consequences on seabed installations (Hovland and Gudmestad, 2001). Offshore petroleum exploration and production involves operations that alter ambient subsurface conditions (changes in stress, temperature and compositions of pore fluids), which in turn, may induce gas hydrate dissociation. For this reason, gas hydrates may be considered as a geohazard for this sector of activity. The consequences of gas hydrate-related seafloor instability to engineering structures would be very damaging such as causing hydrocarbon release from producing well, or seafloor slumping obliterating subsea oil and gas production facilities. The following activities would also trigger gas hydrate dissociation in the sediment:

- Drilling into the sea bottom produces heat that could dissociate gas hydrates in the sediment and release gas. If the free gas released during drilling forms gas hydrates around the wellhead, it could cause a loss of mud density, resulting in wellbore instability and even mechanical system failure. More important gas releases could have consequences  $\mathcal{C}$  the stability of the drilling rig. In addition, excess local pressure caused by as hydrate dissociation in the sediment can induce casing collapse. Sealtoor instability to engineering structures would<br>g hydrocarbon release from producing wen. o<br>ea oil and gas production facilities. The fellov ing<br>ate dissociation in the sediment:<br>into the sea bottom produces heat tha
- Heat from a warm pipeline will propagate in the surrounding sediments. This could cause gas hydrate dissociation, inducing sediment instability and slumping. Under such  $\epsilon_0$ , difficultions, the pipeline may rupture.
- Suction anchors usually used in deep water to keep floating structures anchored to the seafloor would reduce pressure and cause local gas hydrate dissociation, disturbing the friction forces along the walls of the anchor and thus threatening the safety of the operation.

McConnell et al. reviewed the history of gas hydrate shallow hazard assessment and found that low-sature is non-hosted hydrate layers can be safely drilled using existing industry protocols (McConnell et al., 2012). For highly saturated hydrate-bearing sand reservoirs, they will likely continue to be avoided, unless they are the specific targets of the well for methane production.

Mining of hydrates may also cause submarine landslides. Song et al. (2019) applied a thermal-fluid-solid-stress coupling model to NGHD to investigate the failure process of submarine landslides induced by hydrate decomposition. Their results show that hydrate mining may cause settlement of the seafloor and slippage of submarine sedimentary layers to the mining center, and thus can potentially trigger submarine landslides. Based on geophysical and geotechnical data, Zander et al. (2017) investigated the potential impacts of gas hydrate exploitation on slope stability in the Danube deep-sea fan in northwestern Black Sea. Their 2D slope stability model applied to a hypothetical gas

hydrate reservoir suggests that the area is relatively safe against slope failure under static conditions, but probably not sufficiently safe to allow the implementation of infrastructure for hydrate production at the seabed without taking specific mitigation measures into account (*e.g.* relocation options, design criteria).

### **ii. Impact of hydrate decomposition on permafrost**

It has been generally accepted that global warming tends to destabilize gas hydrates present in permafrost through different mechanisms, such as directly melting top layers of gas hydrates (Mienert et al., 2005), thermal shock led by sea level rise (Maslin and Thomas, 2003), and reduction in lithostatic pressure hence hydrostatic pressure due to shrinking of subsea permafrost (Paull and Dillon, 2001; Tinivella and Giustiniani, 2016; Tinivella et al., 2019; Waage et al., 2020; Wallmann et al., 2018). However, the environment in which hydrates are found is different  $\hat{\mu}$  on that encountered on continental margins. In permafrost regions, gas hydrates  $a_n$ <sup>1;</sup> e may coexist with salts, water, and free gas in the offshore sediments, which  $l$  ads to unique characteristics of the ice-hydrate-bearing sediments compared to those of the other marine sediments. However, little work has been done to under tand such properties of permafrost sediments containing gas hydrates, although the mechanical properties of frozen soil and rock in the absence of gas hydrates an  $\Gamma$  r frozen gas hydrate-bearing sediments were extensively investigated (*e.g.* (Arenson et al., 2007; Tsytovich, 1975; Waite et al.,  $2009$ ). The mechanical properties of frozen sand, silt and clay containing tetrahydrofuran (THF) hydrate were determined at  $-10$  °C (Yun et al., 2007), and they found that shearing results in particle rotation, slippage, and rearrangement in the absence of THF hydrates. In contrast, shear force leads hydrates to detach from the mineral surface in the presence of  $\frac{1}{4}$  saturation (<40%) of THF hydrates, or to debond from the sediment grains in  $\mu$  presence of high saturation (>40%) of THF hydrates. The mechanical properties of kaolin clay-ice powder mixtures were investigated in the presence of carbon-dioxide (Liu et al., 2013) and methane hydrates (Li et al., 2016; Li et al., 2019; Luo et al.  $2\sqrt{18}$ ; Yun et al., 2007). The determined shear strength was unexpectedly low  $c_1$  m<sub>pure</sub>d to the sediments containing gas hydrates only, and this was mainly explained by  $t \cdot \epsilon$  lack of cementation between hydrate crystals, ice powders and clay grains. Recently, Yang et al. (2019) reported a set of comprehensive experiments for methane hydrate-bearing frozen sediments. Their results showed that gas hydrates can form micro frames or network structures, resulting in distinctive effects on the mechanical properties (higher shear strength and less brittle under compressional loading) of the simulated hydrate-bearing permafrost sediments compared to frozen sediments in the absence of gas hydrates (Yang et al., 2019). 2019; Waage et al., 2020; Wallmann e. al., 2<br>which hydrates are found is different  $\hat{n}$  on. t<br>gins. In permafrost regions, gas hydrates  $a_1 A^T i e$  m<br>gas in the offshore sediments, which I ads to unic<br>bearing sediments c

Old estimation provided huge volumes (up 9.2 to  $22.3 \times 10^3$  Pg (1 Pg =  $10^{15}$  g)) of methane trapped as hydrates in permafrost of the Arctic regions (Max and Lowrie, 1996). However, more recent studies provided most lower estimates ranging from 27 (~1% of global hydrate estimate) to 800 Pg of methane (Knoblauch et al., 2018; Miesner et al., 2023; Ruppel, 2015). Gas hydrate-bearing permafrost sediments (GHBPS) are sensitive to temperature changes that could be induced by global

warming, seasonal changes, geothermal fluxes, and human activities. Particularly, global warming is causing the shrinking of both terrestrial and subsea permafrost, leading to a reduction in lithostatic pressure and hence hydrate decomposition (Maslin et al., 2010). Scientific research has revealed that global warming has accelerated the rate of ice thawing and gas hydrate decomposition in permafrost regions, and, consequently, led to the release of methane and carbon dioxide into the atmosphere, exacerbating global warming (Andreassen et al., 2017; Portnov et al., 2016). A more detailed review on gas release follows in the next section. This adverse effect of greenhouse gases reaching the atmosphere becomes even more severe in the Arctic regions due to the effect of polar amplification. In other words, the atmosphere or an extensive ocean circulation can lead to heat transport toward the poles. Consequently, climate warming would affect the areas adjacent to the Earth poles at relatively greater magnitude compared to the rest of the Earth surface (Polyakov  $\ge$ t al., 2002), accelerating decomposition of gas hydrates in permafrost regions such as the Arctic. Observations of natural catastrophic events have demonstrated that this mergential negative feedback could tip over the mechanical stability of GHBPS, and trigger a chain of large-scale land and/or seafloor failures, and subsequently induce an abrupt greenhouse gas venting from subsea permafrost in the East Siberian Arctic Shelf (Ruppel and Kessler, 2017) and life-threating events such as tsunamis that could reach the shore of the UK based on evidence of historic events (Long et al.,  $201 \cdot \overline{\text{F}}$  hivella et al., 2019). The instability of GHBPS has been attributed to landslides in Vukon Territory in Canada (Maslin et al., 2010), the permafrost lava observed  $\mathbf{C} \cdot \mathbf{r}'$  e Tien Shan Mountains in China (Marchenko et al., 2007), the formation of massive gas blow-out craters in the northern Barents Sea (Andreassen et al., 2017) and in the Yamal and Gydan Peninsulas in northern Siberia in Russia (Bogoyavlensky et al.,  $20\angle 0$ ). These destructive consequences in recent years are also attributed to the global varning of anthropogenic activities. Based on numerical modeling, Andreassen et al.  $(20.7)$  developed an understanding of how the craters and mounds were formed in the northern Barents Sea and postulated that climate warming leads to the ice sheet retreating, and this is accompanied with catastrophic reduction of the sediment pore pressure. Consequently, gas hydrates initially in permafrost or sediments dissociate. The dissociation of gas hydrates at depth, particularly those underlying impermeable layers, results in building up of overpressure in pores. Finally, when the overpressure reaches a certain threshold, gas hydrate pingos could be formed, and their collapse creates craters in permafrost regions. Furthermore, composition analysis of the gas from such craters showed particularly high concentration of methane (Kvenvolden and Field, 1981). Such high concentration of methane only allows formation of structure I hydrate which makes the gas hydrate-bearing permafrost more vulnerable to global warming. Furthermore, the occurrence of methane hydrates in permafrost layers gives GHBPS more complex characteristics than the sediments containing either ice (*e.g.* hydrate-free frozen soils) or gas hydrates (*e.g.* unfrozen hydrate-bearing sediments). Such characteristics include fluid distribution in pores, unfrozen water content, and ice/hydrate morphologies such as pore filling or grain cementing, load bearing or micro frame structures. At present, there is little knowledge about the physical properties of permafrost sediments that are saturated with variable g would affect the areas adjacent to the Ear'h poles<br>aared to the rest of the Earth surface (Polyakov x al<br>f gas hydrates in permafrost regions such vs th > Ar<br>phic events have demonstrated that th's a creasin<br>he mechanic

ice, hydrate, gas, and saline water (Farahani et al., 2021a, b; Hassanpouryouzband et al., 2020; Yang et al., 2019).

### **4. Gas release from hydrate decomposition**

Figure 2 illustrates the functioning of cold seep areas where the main methaneinvolving biogeochemical processes are presented. It provides some numbers related to methane transport from one compartment to another, storage, and transformations (genesis and degradation) that will be discussed throughout this paragraph.



Fig.2: Conception scheme of biogeochemical processes taking place at hydrate-bearing setting on continental margins with estimated fluxes and stocks. Ranges of microbial methane fluxes (methanogenesis, AOM and AeOM) were converted in mole-to-mass from microbial rates reported and estimated from cited references in Table 2.

Methane venting at the seafloor widely occurs on shelves and continental margins. There, methane and hydrogen sulfide are generated, transported and transformed within the sediment, and part of the former is discharged into the water column (Suess, 2014). At hydrate-bearing settings, the amount of methane that can potentially be released from hydrate decomposition processes is variable and site-specific (Baumberger et al., 2022; Braga et al., 2020; de la Cruz Vargas-Cordero et al., 2021; Ketzer et al., 2020; Marcon et al., 2022; Marin-Moreno et al., 2015; Merle et al., 2021; Meurer et al., 2021; Riboulot et al., 2018; Thatcher et al., 2013). However, judging from the number of articles published in recent years, methane discharge from hydrate decomposition is not a sporadic event (Fu et al., 2021; Hautala et al., 2014; Johnson et al., 2015; Phrampus et al., 2014; Westbrook et al., 2009), and it is likely that this process will further increase in the decades and centuries to come due to climate change.

Once released from the hydrates, methane undergoes several physical and biogeochemical processes, starting from its dissolution in the pore water followed by its oxidation (Figure 2). The remaining methane is transferred into the hydrosphere where it undergoes similar processes. These processes  $a \in \mathbb{R}$  efficient barriers preventing methane transfer to the atmosphere. However, the  $\epsilon$ <sup>t</sup> ciency of these barriers depends on multiple factors (*e.g.* water depth, upwelling flowrate, local current, water stratification, *etc.*); and, at the end, only a sm<sup>-11</sup> portion of the total amount of methane released from NGHD decomposition may reach the atmosphere (de Garidel-Thoron et al., 2004; Ruppel, 2011; Ruppel and Kessler, 2017; Westbrook et al., 2009). Such a transfer occurs particularly in the case of catastrophic releases. and centuries to come due to climate change.<br>
from the hydrates, methane undergoes sev<br>
processes, starting from its dissolution in the p re ve 2). The remaining methane is transferred into the<br>
milar processes. These pro

In the following sections, we discuss in detail the variability of the seafloor methane from hydrate decomposition, followed by the impact of such a leakage on the seafloor ecosystems, seawater chemistry, and the conditions that lead to its transfer to the atmosphere.

#### i. **Flux**, s of methane discharged at the seafloor

Due to the sensitivity of the NGHD to environmental changes, concerns have been raised regarding a massive and prolonged release of methane from hydrate decomposition and its consequences in terms of climate feedback, ocean acidification and ecosystem vulnera bility (Archer, 2007; Biastoch et al., 2011; Garcia-Tigreros et al., 2021). To provide some answers to these societal issues, it is necessary to consider the fluxes of methane released from hydrate decomposition. These fluxes are related to the rate of hydrate decomposition, which depends on multiple factors. For outcropping hydrates, the main factors are the flow velocity of the contacting methane-free water, the extent of partial-sediment cover, and the presence of oil film or biofilms and nonmethane guest molecules. Considering hydrate-bearing sediments, the porosity, thickness and thermal properties of the sediment are key factors affecting build-up and flow of methane-charged fluids until its release at the seabed; and these flow-driving factors depend on both the free-gas and hydrate saturation levels that evolve over the course of the decomposition.

Although hydrates are widespread on continental margins and in the permafrost, and were intensively investigated in the former location, there are few natural sites where hydrate decomposition has been quantified (Tables 1 and 2). The rate of hydrate

dissolution has been determined in the Cascadia Margin (Heeschen et al., 2005; Hester et al., 2009; Lapham et al., 2010; Linke et al., 1994; Riedel et al., 2010; Römer et al., 2016; Suess et al., 1999; Torres et al., 2002; Wilson et al., 2015), the Gulf of Mexico (Lapham et al., 2014; Solomon et al., 2008) and the Monterey Bay (Rehder et al., 2004). The data, either measured or calculated from other measured parameters, revealed high variabilities not only from one region to another, but also within a given geological setting (Table 1). Thus, for studies undertaken in the Cascadia Margin the dissolution rate ranges between 29 to  $7.9x10^6$  mmol.m<sup>-2</sup>.yr<sup>-1</sup>. Lowest values were obtained for deposits characterized by thermogenic hydrates trapping multiple guest molecules, and/ or oil film covering the outcropping specimens as the presence of such cover significantly mitigates the dissolution rate. Lapham et al. (2014) showed that the aforementioned range of dissociation rates is similar to previously reported laboratory measurements (Bigalke et al., 2009). In the Gulf of Me $\cdot$ ico, Lapham et al. (2014) measured a dissolution rate of  $6.6x10^6$  mmol.m<sup>-2</sup>.yr<sup>-1</sup> for thermogenic hydrates. Such a rate for thermogenic hydrates is in the same order of magnitude than the value of  $4.7 \times 10^6$  mmol.m<sup>-2</sup>.yr<sup>-1</sup> obtained by Hester et al (2009) a Ba kley Canyon, and it is in the same range than the rate range of 8-  $9.5 \times 10^6$  mmol.r<sup>2</sup>.yr<sup>-1</sup> (141-167 cm.yr<sup>-1</sup>) measured from synthetic methane hydrates brought at the seafloor for *in situ* decomposition experiments (Rehder et al., 2004). Furthermore, Figalke et al. (2009) performed laboratory-based experiments at temperature and pressure conditions within the hydrate stability field to investigate the dissolution of methane hydrates in undersaturated seawater. The dissolution rate was found to be strongly dependent on the friction velocity and the temperature of the sequence turbulent flow, showing that hydrate dissolution in undersaturated seawater is  $\gamma$  diffusion-controlled process. They suggested that additional experimental work is required to address the dissolution kinetics of nonpure methane hydrates, as both,  $\lambda$  solubility limit and the understanding of the molecule transfer processes at the phase boundary during dissolution, are less well constrained. It is also importa<sub>nt</sub> to note that the measurement principles, the instruments and the computing approach, s used for these aforementioned studies of *in situ* hydratedissolution may differ from one research group to another, leaving bias in the comparison. Bigalke et al., 2009). In the Gulf of Me. i.co, Lolution rate of  $6.6x10^6$  mmol.m<sup>-2</sup>.yr<sup>-1</sup> for the n. a.g. equited by Hester et al. (2009) a Ba kley Ca the rate range of  $8-9.5x10^6$  mmol.n<sup>-2</sup>.yr<sup>-1</sup> (141-16 methane h

Moreover, methane hydrate dissolution rate depends on the thickness of the diffusion boundary la er and the methane concentration in water, and this second parameter is in turn controlled by the solubility of methane. Rehder et al. (2004) showed that gas hydrate dissolution rate depends on the difference between the local solubility in the presence of gas hydrates and the local dissolved-phase concentration of the hydrate-forming gas. Lapham et al. (2010 and 2014) measured the methane concentration in sediments immediately surrounding outcropping deep-sea gas hydrates for two sites in Barkley Canyon and the Gulf of Mexico, respectively. Their results showed that pore-fluids are significantly under-saturated with respect to expected values at equilibrium with methane hydrates, indicating that the hydrates should continue to dissolve. They also showed that dissolution rates calculated from *in situ* methane concentration gradients are significantly lower than those predicted for methaneundersaturated pore water in direct contact with pure methane hydrates if equilibrium methane concentrations exist immediately adjacent to the hydrate surface. Lapham et al. (2010) suggested that the factors that retard hydrate decomposition in sediments here

could be oil coating or biofilms. This is supported by Wilson et al. (2015) who investigated how that sediment cover can affect hydrate dissolution by means of field (at Barkley Canyon) and laboratory measurements. The dissolution rate of outcropping thermogenic hydrates covered with sediment was around  $3.4 \times 10^3$  mmol.m<sup>-2</sup>.yr<sup>-1</sup> (<1 cm.yr<sup>-1</sup>), whereas that of synthetic hydrates exposed directly to bulk water was an order of magnitude higher. Their results are in agreement with dissolution-rate values calculated by Riedel et al (2010) for buried hydrates at sites on the Clayoquot Slope of the Cascadia margin. Thus, as hydrate dissolution is mainly controlled by diffusion, the presence of sediment slows the rate of molecular diffusion via porosity/tortuosity effects.

For its part, hydrate dissociation has been investigated at the high latitude regions such as the Western Svalbard (Ferre et al., 2020; Marin-Moreno et al., 2015; Marin-Moreno et al., 2013; Thatcher et al., 2013; Westbrook et al., 2009), the U.S. Beaufort margin (Phrampus et al., 2014) and the Laptev Sea (Chernykh  $f(\vec{x})$ , 2020); as these regions are very sensitive to temperature increase due to climate change (Hassol, 2004; Hassol and Corell, 2006). Investigations on the U.S. Atlantic margins also suggest that multiple methane emission sites are partly related to hydrate dissociation due to the sea-bottom temperature increase (Phrampus and Hornbach, 2012; Skarke et al., 2014; Weinstein et al., 2016). However, as it is relatively usual to observe gas emissions associated with hydrates at cold seeps, this coexistence makes it difficult to accurately assess the contribution of hydrate dissociation in the total gas discharge. The dissociation process requires bringing the pressure and  $\ddot{\cdot}$  operature conditions of the deposits to the boundary of the GHSZ to allow the formation of gas bubbles, and the common factor amongst the aforementioned sites  $\frac{1}{2}$  the occurrence of intense gas emissions at the upper limit of the GHSZ. Nevertheless, ike for hydrate dissolution, Table 2 shows that the estimated methane fluxes and the potential discharge trajectory are highly heterogeneous. In one of the first estimates, Wesbrook et al (2009) estimated that  $\sim 20$ Tg.yr<sup>-1</sup> of methane can be released from hydrates over an area of 22,300 km<sup>2</sup> corresponding to a swath within 360-400 m water depth nearly all around the Svalbard archipelago. Marin-Moreno et al (2013 and 2015) also investigated the sensitivity to climate change of  $\mu$ , nydrate deposit present in the Western Svalbard continental margin by considering a temperature-increase path following either the lower  $(2.6)$  or the upper (8.5) cases of the Representative Concentration Pathways (RCP). Their projection indicated that  $0.029$ - $0.053$   $Tg.yr^{-1}$  of methane can be released from hydrate dissociation over an area of  $\sim$ 134 km<sup>2</sup> during the next three centuries. Such a projection is also in agreement with the estimates of 22.4 Tg.  $yr^{-1}$  proposed by Ferré et al (2020) along the 360 m isobaths at the Norwegian–western Svalbard Margin. By extending to the swath width of Svalbard archipelago corresponding to 400-500 m water depth (swath width complementary to the one considered by Wesbrook et al., 2009), Marin-Moreno et al. (2013 and 2015) showed that the methane discharge may reach 1.7-9 Tg.yr<sup>-1</sup> over 41,400 km<sup>2</sup>. Thus, their estimates of vulnerable hydrates are more than twice smaller than the estimate obtained by Wesbrook et al (2009) for a surface area three times larger but located at deeper depth. Their results also showed that hydrates remain stable beyond 500 m water depth. Such studies illustrate the importance of the water depth (hydrostatic pressure) on the stabilization of hydrates. It is very interesting France dissociation has been investigated at tr? high<br>Svalbard (Ferre et al., 2020; Marin-Moreno et al., 20014) and the Laptev Sea (Chernykh  $\epsilon$ ,  $\epsilon$ ,  $\epsilon$ ,  $\epsilon$ ,  $\epsilon$ ),  $\epsilon$ ) tensingations on the U.S. Atlantic manging

to mention that they found that the choice of the RCP scenario has a small impact on the total discharge. The calculated methane fluxes off Svalbard ranges from an estimated average of 2 mmol.m<sup>-2</sup>.yr<sup>-1</sup> (Thatcher et al., 2013) to 13.5 mol.m<sup>-2</sup>.yr<sup>-1</sup> calculated by Marin-Moreno et al (2013). The fluxes calculated by Phrampus et al. (2014) fall within this range of values for the U.S. Beaufort margin  $(0.88 - 4.4 \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1})$ , whereas values up to two and three order of magnitude higher were obtained by Skarke et al (2014) and Chernykh et al (2020) on the U.S. Atlantic margin and in the Laptev Sea, respectively.

Moreover, it is important to recall that these methane fluxes are not constant over the time; and therefore, there is a need to take into account processes and seasonal changes that induced short to long-term variations that affect annual fluxes such as tides (Römer et al., 2016; Sultan et al., 2020), seismic activities (Fischer et al., 2013; Franek et al., 2017; Lapham et al., 2013) and temperature (Berndt et al., 2014; Ferre et al., 2020).





# for complex thermogenic hydrates, \* for synthetic hydrates,  $\pi$  for buried hydrates (otherwise it is outcropping hydrates)

Table 2: Free methane fluxes measured from field study of hydrate dissociation and over a hydrate deposit





## ii. Microbial processes and methane discharge at the **seafloor**

Currently global methane emissions are about 500-600 Tg per year (Ehhalt et al., 2001; Saunois et al., 2020) (see section 4.iv "Transfer to the atmosphere"), with around  $70\%$  $(350-400)$  Tg) of which is due to methanogenesis from a wide variety of habitats including anoxic seafloor econversions (Conrad, 2009). Around 40% of the methane produced by methanogenesis escapes to the atmosphere (Lyu et al., 2018). In marine sediments, microbial nett anogenesis produces methane through the terminal anaerobic breakdown of organic matter deposited on the seafloor (Parkes et al., 2014; Wellsbury et al., 2000) (Fig.2). Estimations suggest that  $3-18\%$  of the buried organic carbon within the seafloor is converted to  $CH_4$  by methanogenesis in continental margin (Egger et al., 2018; Xu et al., 2022). Recent estimates from Xu et al. (2022) indicates that the global methanogenesis budget approximates 13 Tg of methane per year. Methanogenic activities have been observed from surface to deep sub-seafloor sediments (Table 3).

Table 3: Rates of methanogenesis, anaerobic methanotrophy (AOM) and aerobic methanotrophy (AeOM) in various microbial marine habitats.

	<b>Methanogenesis</b>	Anaerobic methanotrophic oxidation	Aerobic methanotrophic oxidation
Sediments:	$0.02$ to 30 nmol cm <sup>-3</sup> d $1******$	$5.1 \times 10^{-8}$ to 7.0 x 10 <sup>4</sup> nmol $cm^{-3} d^{-1***}$	3.4 x $10^{-8}$ to 1.1 nmol cm <sup>-3</sup> d $1****$
-with hydrate	$0.1 - 2.73$ nmol cm <sup>-3</sup> d $1***$	$10^2$ to 5x10 <sup>3</sup> nmol cm <sup>-3</sup> d <sup>-1</sup> $1******$	$10-12$ mmol m <sup>-2</sup> $\overline{d^{-1}}$



\* Estimation of microbial methane production rates in deep marine sediment at hydrate ridge is based on representative species of methanogen *Methanoculleus submarinus* starved in culture with Biomass Recycle Reactor coupled to quantitative PCR of *mcrA* gene abundances (Colwell et al., 2008). \*\*Vigneron et al., 2015, Cold seeps at Guaymas Basin in Sonora margin; \*\*\*Wellsbury et al., 2000, Blake Ridge; \*\*\*\*(Gao et al., 2022). \*\*\*\*\*(Parkes et al., 2007) and (Newberry et al., 2004) \*\*\*\*\*\*Boetius and Wenzhöfer, 2013. The < sign indicate underlying uncertainties.

The formation of methane involves a group of strictly anaerobic archaea called methanogens. However, smaller amounts of methane are produced from methylphosphonates in oxic waters by both phytoplanktons with mainly Cyanobacteria and Thaumarchaea (Bižić et al., 2020; Klintzsch et al., 2019; Metcalf et al., 2012). Methanogens use various low-molecular-weight catabolic substrates for biosynthesis of methane, and thus the rate of methanogenesis can be  $\sqrt{t}$  if  $\frac{dt}{dt}$  with to estimate. The Redox reaction of dihydrogen  $(H_2)$  with carbon dioxide  $\langle CO_2 \rangle$  and/or with formate are considered as the main substrates for methanogenesis in marine sediments (Newberry et al., 2004; Parkes et al., 2007). However, it has been shown that acetate can become the dominant substrate in deeper sediments (Ree<sup>t</sup>  $\psi$  g'), 2007). Methanogens also performed methanogenesis with methylated compounds. Methylotrophic methanogenesis may be an important methane source in coast also lallow sediment (Conrad, 2020). Acetate and other potential substrates for microbial  $\mu$  thanogenesis could derive from either thermal alteration or biological degradation of organic matter. Recent developments in high throughput sequencing techniques  $\lambda$  are revealed an unexpected larger diversity within the methanogens and suggest  $t_{n}$ , the metabolic pathway is one of the most ancient on Earth (Vanwonterghem et al., 2016; Wang et al., 2021). Metagenome assembled genomes (MAGs) of potential methanogens suggest the acquisition of both novel functions in activation  $C<sup>c</sup>$  alternative catabolic substrates such as short and medium chain of alkanes and volatile fatty acids (Laso-Pérez et al., 2019; Wang et al., 2021), and in derivation of  $\chi$ -lular energy from methoxylated aromatic compounds from lignin occurring in coal bed (Inagaki et al., 2015; Kurth et al., 2021). The overall rates of methanogenesis in marine sediments range from 0.02 to 30 nmol cm<sup>-3</sup>  $d^{-1}$  (Table 3) (mole-to-mass conversion is 0.32 to 480 ng cm<sup>-3</sup>  $d^{-1}$  reported in Figure 2). However, microbial rates are limited and restricted to discrete habitats and mostly obtained in incubation with radiotracers in laboratory conditions and ambient pressure. Thus, the extrapolation to estimates of global microbial methane production and consumption per year may be subjected to high uncertainties. All the methanogenesis pathways lead to the production rate of 5-33 Tg of methane  $yr^{-1}$  in continental marine sediment at global scale (Wallmann et al., 2012). However, the transfer of this amount of methane generated from the seabed along continental margins to the atmosphere is efficiently buffered and controlled by both aerobic (AeOM) and anaerobic oxidation of methane (AOM), respectively at and below the oxic-anoxic interface of the sediment and water aates in oxic waters by both phytoplanktons ith n<br>aea (Bižić et al., 2020; Klintzsch et al., 2019; M<br>e various low-molecular-weight catabolic self-strate<br>us the rate of methanogenesis can be liffi ult to tydrogen (H<sub>2</sub>) w

columns (Reeburgh, 2007) (Fig.2). These two oxidation processes can be expressed as follows:

$$
CH4 (aq) + 2O2 (aq) \rightarrow CO2 (aq) + 2H2O
$$
 (AeOM)  
\n
$$
CH4 (aq) + SO42 (aq) \rightarrow HCO3- (aq) + HS- (aq) + H2O
$$
 (AOM)

AeOM occurs into the geosphere at cold seeps and hydrothermal fields from a symbiotic association between specific methane-oxidizing bacteria with marine animals (Petersen and Dubilier, 2009). In the water column, AeOM represents the final sink for methane before reaching the atmosphere. Within the anoxic sediment, AOM is a microbial-mediated process that occurs within the geoclemical horizon commonly called the sulfate-methane transition zone (SMTZ) where  $v_r w_a$ . I diffusion of methane reacts with downward diffusing seawater sulfate (Borowski et al., 1996, 1999; Gao et al., 2022; Hinrichs and Boetius, 2002; Pohlman et al. 2008). Laboratory experiments from natural samples have shown that the overall  $i_{\alpha}$  tes of AOM in marine sediments coupled to sulfate, metal oxides and nitrite/nitrate *is* electron acceptors range from 5.1 x  $10^{-8}$  to 7.0 x  $10^4$  nmol cm<sup>-3</sup> d<sup>-1</sup> (Gao et al., 2022,  $7a$  ie 3) (mole-to-mass conversion is 81.6 x 10<sup>-8</sup> to 112 x 10<sup>4</sup> ng cm<sup>-3</sup> d<sup>-1</sup> reported in Figure 2). Predicted global rates of AOM based on the regression model with diffusive  $f(x)$  axes of CH<sub>4</sub> suggest that 45-61 Tg of methane are oxidized annually; corresponding to  $\sim$ 3-4% of the organic debris deposited on the seabed (Egger et al., 2018). On a global scale, 8 to 65 Tg of methane per year bypasses the two aforementioned redimentary biofilters and is released in the water column (Saunois et al., 2016;  $S^{\dagger}$  is et al., 2015). This estimate is not restricted to hydrate decomposition only as it is difficult to decipher, but involves several methane pools, including free methane generated either from thermal cracking at deep depth or shallow methanogenesis. ded process that occurs within the geocl emical<br>e-methane transition zone (SMTZ) where  $v_T v_{\alpha}$  and<br>nward diffusing seawater sulfate (Borows  $\alpha$  e.g. al.,<br>ths and Boetius, 2002; Pohlman et al. 20. 8). Lat<br>mples have sho

Methane released from  $h_y$ , trate decomposition affects the transport of chemical species within the sediment overlaying the deposits by generating a continuous carbon flux that represents an energy supply for the benthic chemosynthetic assemblages (Niemann et al., 2006). Such an energy supply stimulates the seepage-associated ecosystems located in the sediment as well as in the water column (Boetius and Suess, 2004; Marcon et al., 2014; Sahling et al., 2002; Suess, 2014) and gives rise to the following consequences:

 **Formation of interface horizons shaped by redox processes**. The microbial processes and the community diversity that characterized them are often stimulated at discrete subsurface geochemical interfaces (Parkes et al., 2014), creating a zonation within the sedimentary column. From a biogeochemical viewpoint, anaerobic methane oxidation, methanogenesis from acetate and Hydrogen/ Carbon Dioxide, acetate oxidation, sulfate-reduction, and bacterial productivity were stimulated in both the hydrate and the free-gas sediment horizons beneath compared to hydrate-free sediments (from 1.5 to 15 times higher) at the Black Ridge setting in NW Atlantic Ocean (Wellsbury et al., 2000) and surface sediment of the Cascadia Margin in the North Pacific Ocean (Cragg et al., 1995); and distinct microbial communities dominated the former sedimentary environments. Estimations of microbial methane production rate ranged from 0.015 to 0.62 nmol  $cm^{-3}$  d<sup>-1</sup> in sediments without hydrate to 0.1 to 2.73 in methane hydrate bearing sediments (Table 2) (mole-to-mass conversion of methane production rates in hydrate bearing sediments were 1.6 to 43.68 ng  $\text{cm}^{-3}$  d<sup>-1</sup> reported in Figure 2). Thus, the cell numbers as well as the microbial activities involved in the methane cycle (methanogenesis and anaerobic methanotrophy) strongly increase within the sedimentary geochemical-horizons, thus increasing the amount of hydrates and associated free gas (Dickens and Quinby-Hunt, 1997; Wellsbury et al., 2000). At the Black Ridge hydrate-setting, the total microbial number is significantly higher around the Bottom Simulating Reflector (BSR), especially beneath it within the  $\mu$ -e-gas or dissolved-gas occurrence zone (Wellsbury et al., 2000). Indeed, the potential rates of microbial activity increase at the interface between the BS $\lambda$  and the free-gas zone beneath, mainly towards the free-gas zone (Cragg  $\pm$  al., 1996; Cragg et al., 1995; Wellsbury et al., 2000). Thus, the presence  $\epsilon^f$  is equal associated with hydrate deposits rather than free gas-depleted hydrates, impacts on the microbial activities including methane and aceta<sup> $\cdot$ </sup> metabolisms. At the SMTZ, pore water methane and sulfate are consumed  $t h \cdot u \rho$  the AOM by syntrophic consortia of anaerobic methanotroph archae.  $(A, \text{ME})$  and sulfate reducing bacteria (SRB). The depth of the SMTZ is strongly affected by the intensity of the methane flux, while its state (steady or transient) is rather linked to the flux variations over time (Borowski et al., 1999; <sup>4</sup>e Prunelé et al., 2017; Jørgensen and Kasten, 2006; Kasten et al., 2003). A recent investigation of site located at the rim of a hydrate-bearing zone of  $\sim$  s albard has shown that nonvertical methane transport can significantly affect the gas migration pathway, leading to the occurrence of double SMTZs and enable microbial distribution within the sediment (Treude et al., 2020). Previous studies have shown that the settlement of the SMTZ starts around  $10^{\circ}$  to  $1/00$  years after the inception of gas hydrate dissociation (Argentino et  $\alpha'$ ., 2021; de Prunelé, 2015; de Prunelé et al., 2017; Hong et al., 2016; Pape et al., 2020; Sultan et al., 2016). The SMTZ depth is controlled by the diffusive fluxes of methane and sulfate, which depend on continuous decrease in the reactivity of organic matter with the increasing sediment depth and therefore the age of the sediment (Borowski et al., 1999). The sedimentation rate and the associated organic matter burial flux are the key control factors to define the depth of the SMTZ (Egger et al., 2018). These two factors depend in turn on the water depth, the distance from land and surface biological productivity in the overlying water column. Human alteration of nutrient loading and oceanographic regimes due to global warming can also impact on the SMTZ distribution in sediment (Egger et al., 2018). microbial number is significantly higher are und the (BSR), especially beneath it within the  $1.2e^{-2}$  ce zone (Wellsbury et al., 2000). Indeed, the pt tent ncrease at the interface between the BSX a. d the frowards the f

 **Ecosystems-hosted methanotrophy**. Microbial consortia of anaerobic methanotroph archaea and sulfate-reducing bacteria are not restricted to gas hydrate-bearing sediments (Boetius et al., 2000), but are widely distributed in other marine environments including cold seeps (Hinrichs et al., 1999; Vigneron et al., 2013), mud volcano (Lazar et al., 2011), deep hypersaline sediments (La Cono et al., 2011) and hydrothermally impacted sediments (Holler et al., 2011; Teske et al., 2002). The major controlling factors for the ANME population distribution are the availability of methane and sulfate, or known alternative electron acceptors such as nitrate, iron or manganese (Wallenius et al., 2021). ANME is believed to use a process of "reverse methanogenesis" biochemical pathway and are phylogenetically related to methanogenic lineages. The doubling time of ANME/SRB consortia, estimated to approximately seven months under controlled *in vitro* conditions (Nauhaus et al., 2007), suggests that the set-up of an efficient AOM microbial filter in sediments would be on the order of decades (James et al., 2016). The coupled process of AOM and sulfatereduction increases alkalinity, promoting the precipitation of authigenic carbonate by reacting with the seawater calcium (Luff and Wallmann, 2003). This authigenic carbonate precipitation results in  $\alpha$  decreasing of the sediment porosity that changes the fluid flow pattern, and in turn affects the supply of methane at the SMTZ (Steeb et al., 2014). At Hydrate Ridge in the Cascadia margin subduction zone, carbon volume  $e^{i\phi}$  nations suggest that 14% of the oxidized methane is sequestered into this seafloor mineral. Thus, carbonate mounds may represent a significant wet allet and sink in deep-sea (Marlow et al., 2021; Marlow et al., 2014). Nat  $\sim$  l  $\sim$  d anthropogenic methane seepages into an oxygenated water column stimulate the distribution, abundance and activity of aerobic methanotrophic bacterial populations (Rogener et al., 2018; Steinle et al., 2015). The AeOM reaction hinders the methane transfer to the atmosphere by converting it into bion.as or dissolved inorganic carbon; which in turn could affect the pH in the ocean (Biastoch et al., 2011). Estimations of aerobic methanotrophic oxidation rates in oxygenated sediments ranged from 3.4 x  $10^{-8}$ to 1.1 nmol of  $C_1$ <sup>T</sup> cm<sup>-3</sup> d<sup>-1</sup> (Table 2, Gao et al., 2022) (mole-to-mass conversion is  $5^{\frac{1}{4}} \times 10^{-8}$  to 17.6 ng of CH<sub>4</sub> cm<sup>-3</sup> d<sup>-1</sup> reported in Figure 2). decades (James et al., 2016). The coupled process<br>
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**Temporal and spatial dynamics of (micro)-biological communities**. The methane concentration and flux strongly affect the diversity of the chemosynthetic communities such as sulfur bacterial mats, tubeworms, and clams that are settled on the seafloor (Fischer et al., 2012; Pop Ristova et al., 2012). These chemosynthetic seep fauna are therefore bioindicators of AOM activity and methane flux. Thus, macrofauna colonies such as vesicomyid clam populating the *Beggiatoa* mats (filamentous microbes) settled on methane hydrate-bearing sediments consist nearly exclusively of endemic species and are found in higher density at seeps and hydrothermal vents compared to non-seep environments (Sahling et al., 2002). The methane fluxes may vary on very large spatial scales as a consequence of factors such as the variation of the rate of hydrate decomposition or carbonate precipitations, or after a submarine mud eruption, a continental slope sliding, and even an earthquake. Thus, large expulsions of fluids and mud from active submarine volcanos may strongly affect the distribution of communities; sometimes causing their extinction.

However, long-term observation after such large expulsions of fluids also indicates a resilience of the ecosystem to recover the main microbial function. For instance, the re-colonization of complex pioneer microbial populations composed of aerobic and anaerobic methanotrophs were observed several years after a subsurface mud eruption at the active center of the Häkon Mosby mud volcano (Ruff et al., 2019).

Predicting how climate change will affect the aforementioned microbial processes remains elusive. Several studies have claimed that microbial methane production may be enhanced by global warming. In fact, methanogens are active in most habitats where temperature ranges from 0 to 122°C (Hoehler et al., 2018). In marine sediments, the methanogenesis process is restricted to either the sediment 'aver deep below the SMTZ (meter to tens of meters) and used acetate and hydrogen, or in writicial sediment  $(\leq 1 \text{ m})$ where non-competitive substrates such as methanol and other methylated compounds are available. Interestingly, the coexistence of sulfate-reduction and methanogenesis also occur in shallow sediment when methylotrophic pathway to produce methane takes place (L'Haridon et al., 2014). Methanogen distribution may be limited by competition for acetate and dihydrogen and are rapidly out-completed by sulfate-reducers for these same substrates. In shallow sulfate-rich sediments, methanogens utilizing noncompetitive substrates such as methylated  $\partial^m$  es could meet the substrate requirements of sulfate-reducing bacteria. Thus, variation of *in-situ* temperature in marine sediments can strongly impact methane production pathways via biochemical, bioenergetic and/or ecological mechanisms (Conrad, 2020; Hoehler et al., 2018). Temperature increase positively impacts methanogenesis activity (Maltby et al., 2018), resulting in higher methane production with potential higher emission budget to the hydrosphere. In fact, a warming of bottom water may result in increasing the amount of methane contained within the shallow sediments and eventually lead to the shoaling of the  $SMTZ$  in vast areas of the continental she<sup>14</sup>. Even if representative isolated microbes grow within a wide range of temperatures in the laboratory, changing global temperatures may also shift the diversity of the nicrobial community towards more responsive and efficient microbial metabolisms at higher *in situ* temperature. process is restricted to either the sediment 'aver def meters) and used acetate and hydrogen, or in . wrfinetitive substrates such as methanol and othe meterestingly, the coexistence of sulfat -re, uction allow sediment w

Moreover, the lifetime of methane in the water column is longer when it is transferred from the seafloor as bubbles, partly because microbes use dissolved methane. The aerobic oxidation of methane by free-living and symbiont-associated bacteria occurs on the seafloor and within water column at sites where free methane is released (Levin, 2018; Steinle et al., 2015; Sweetman et al., 2017). Accordingly, hydrate dissociation may affect the water column even more than hydrate dissolution. If the methane hydrate dissociation is fast enough and releases large quantities of gas, part of it will escape the function of the microbial filter, as it will not be accessible by the microorganisms. However, additional methane loss prior to reaching the atmosphere occurs as bubble stripping, *i.e.* dissolution in the surrounding water, or replacement by oxygen, nitrogen or other dissolved gases in the water masses. Such a gas exchange may not be complete over a short distance, and thus a significant methane fraction would be transferred to the

atmosphere at shallow water depth. The amount of methane bypassing sedimentary benthic biofilters, entering in the water column, and transfer to the atmosphere can vary widely depending on the type of water and specific environmental conditions. For coastal and marine environments, estimation is challenging due to complex interactions between sediments, water column and the atmosphere. Therefore, it is difficult to provide depth threshold from which sedimentary methane is transferred to the atmosphere. McGinnis et al. (2006) studied methane emissions in the Black Sea and showed that significant transfer to the atmosphere occurs at water depth shallower than 100 m. Other studies highlighted the coastal region located in water depth ranging between ~0 and 50/ 75m, where gas hydrates are not stable, as being by far the more important contributor of sedimentary methane to the atmosphere (Mao et al., 2022; Michel et al., 2021; Römer et al., 2021; Weber et al., 2019). In a recent study, Joung et al.  $(2022)$  investigated the transfer of methane from the seafloot to the sea surface along the US margins at seep areas including hydrate-bearing sites, both in the Atlantic and Pacific sides. They results showed no occurrence of such a vertical transfer at water depth deeper than 430m, which is shallower than the upper boundary of the hydratestability field (Joung et al., 2020; Joung et al., 2022). In addition, during the aerobic oxidation of methane in the water column, bacteria produce biomass and/or carbon dioxide, which latter is dissolved in the seawater. Large production of carbon dioxide may contribute to the decrease of the water  $p<sub>A</sub>$ , and lead to local ocean acidification as mentioned in section 4.i. Biastoch et  $\partial^1$  ( $\partial$ 0.<sup>1</sup>) estimated that the oxidation of methane discharged in the Arctic Ocean within the next centuries will result in a drop of 0.25 pH units and a local decrease of up to  $25\%$  of the oxygen concentration. A bloom of aerobic methanotroph communities in response to the large-scale methane release may happen, creating a vertical stratification  $\vec{c}$  aerobic methanotrophs consuming the dissolved oxygen and depleting the amount of oxygen in the water column. Such a microbial bloom has been observed from the Deep Water Horizon blowout in the northern Gulf of Mexico, which has increased methane oxidation rates in the water column compared to natural methane seepage ( $\kappa$ ogener et al., 2018). 121; Komer et al., 2021; Weber et al., 2019) In a regarded the transfer of methane from the seafloo. to at seep areas including hydrate-bearing s tes, botthey results showed no occurrence of 'alci. a vertian 430m, which i

### **iii. Marine methane transfer to the atmosphere**

After  $CO<sub>2</sub>$ , atmospheric methane is the second most important climate-forcing trace gas driven by anthropogenic sources. Its burden in the atmosphere has drastically increased by 150% since the pre-industrial era and is currently rising at a high rate (Nisbet et al., 2014; Nisbet et al., 2016; Platt et al., 2018). Our understanding on the respective contribution from its different natural sources and sinks remains incomplete (Kirschke et al., 2013; Saunois et al., 2016; Saunois et al., 2017; Saunois et al., 2020). Top-down and bottom-up studies show that natural processes emit between 218 and 371 Tg CH<sup>4</sup>  $yr<sup>-1</sup>$  on average, respectively (Saunois et al., 2020).

Aquatic methane enters the atmosphere either as bubbles rising from the seafloor or by diffusion from saturated waters across the sea-air interface. Early estimates by Lambert & Schmidt (1993) provided a marine source to the atmosphere of 3.5 Tg CH<sub>4</sub> yr<sup>-1</sup> and predicted that the open ocean might become a sink at atmospheric concentrations equivalent to today's concentrations (Lambert and Schmidt, 1993). That prediction did

not materialize. Survey of the global ocean  $\Delta CH_4$  data combined with estimates of ebullitive fluxes found a range of  $6-12$  Tg CH<sub>4</sub> yr<sup>-1</sup> (Weber et al., 2019). It is generally admitted that seafloor emissions reach the atmosphere only at shallow depth (continental shelf and upper slope), whereas in the open ocean methane flux correlates with net primary production and would therefore be mainly produced *in situ* by organic matter cycling (Weber et al., 2019). Rosentreter et al. (2021) further extended the study of Weber et al (2019) to sources from coastal ecosystems, and estimated a median flux of 8.4 Tg CH<sub>4</sub> yr<sup>-1</sup> (interquartile range 4.8–28.4 Tg CH<sub>4</sub> yr<sup>-1</sup>) (Rosentreter et al., 2021) (Fig.2). These estimates can separate emissions from seafloor reaching the atmosphere on one side with *in situ* production on the other side. However, atmospheric estimates are based on measurements that do not discriminate whether sedimentary methane has been buffered in methane hydrates that eventually decomposed or is a direct emanation of methane from seeps.

Focusing on submarine seeps only, Etiope et al. (2019), compiling the available literature, estimated the methane transfer from the geosphere to the atmosphere at 3.9 Tg CH<sub>4</sub> yr<sup>-1</sup> with a maximum potential value of 9  $Tg$  C<sub>H<sub>4</sub> yr<sup>-1</sup>. In this synthesis, all</sub> sources were located at depths shallower than  $500 \ldots$ . The main emitting area is the East Siberian Arctic Shelf with 2 Tg CH<sub>4</sub> yr<sup>-1</sup> (range 0-4 Tg CH<sub>4</sub> yr<sup>-1</sup>, (Berchet et al., 2016)). Etiope et al.'s estimate is nearly  $\pm$  ice lower than a previous geological estimates of 20 Tg CH<sub>4</sub> yr<sup>-1</sup> (Judd, 2004; *K* vervolden et al., 2001). There, offshore direct sources account for 5-20 Tg CH  $\gamma$ .<sup>-1</sup> and hydrate dissociation around 0-5 Tg CH<sub>4</sub>  $yr^{-1}$ .

Numerous investigations on the consequence of methane release from hydrate decomposition during past climate change such as the Paleocene-Eocene thermal maximum argued that these events have contributed to an increased injection of methane into the atmosphere  $\vec{t}$  at moderately accelerated climate change (Dickens et al., 1997; Kennett et al., 2003; McInerney and Wing, 2011; Norris and Röhl, 1999). Such an impact involves a huge  $a$  vount of methane passing through the entire water column to reach the atmosphere. Several modelling and simulation studies explored the interactions between even dissociation and climate change (Archer, 2007; Ruppel and Kessler, 2017 and references therein). Most of these studies found moderate release of methane to the atmosphere under the worst climate scenario (RCP 8.5) (Biastoch et al., 2011; Hunter et al., 2013; Kretschmer et al., 2015). Kretschmer et al. (2015) estimated that up to 4.73 Tg CH<sub>4</sub> yr<sup>-1</sup> could be released on average, ignoring potential oxidation in the water column. This is comparable to today's global ocean methane sources, a minor term in the global annual methane budget. They also noted the importance of the uncertainty associated with the inventory of hydrates in the sediment within the GHSZ. Serov et al. (2017) highlighted the importance of understanding the post-glacial history of present-day gas hydrate provinces to better predict the trajectory of their destabilization. It is also important to assess the role of anthropic activities on the vulnerability of NGHDs. Indeed, although several studies investigated the monitoring of marine methane emissions from oil and gas wells (Böttner et al., 2020), there is no study related to human-induced destabilization of NGHD from seafloor or sub-seafloor resource extraction. To our knowledge there is no literature dealing with It methane hydrates that eventually decompted or<br>
seeps.<br>
Ubmarine seeps only, Etiope et al. (20.9), some ated the methane transfer from the get sph re to the<br>
that a maximum potential value of  $9 \degree$  g  $\degree$  g  $\degree$  f4 yr<sup>-</sup>

the quantification of methane leaks during production tests from hydrates and its fate, nor on its impact on the associated ecosystems over time. As mentioned previously, the water column acts as a relatively efficient but still poorly characterized oxidative-barrier to prevent seafloor methane from reaching the atmosphere. Therefore, continuous efforts driven by field-based quantitative approaches are needed to achieve an in-depth understanding of the transfer and fate of gases in the different Earth compartments, as well as to identify under which circumstances marine methane reaches the atmosphere. Thus, the assessment of the physical and biogeochemical processes related to methane in the water column and its probability to reach the atmosphere remains timely and challenging.

Besides, like seafloor methane emissions, methane transfer from the ocean to the atmosphere is influenced by environmental factors such as seasonality. Experiments showed that strong vertical density gradients in the water column developed during the warm season might limit the ascent of methane gas to the  $s$ -a surface and its release into the atmosphere. During winter, the vertical mixing in the water column is enhanced and consequently more methane is released into the atmosphere (Gentz et al., 2014; von Deimling et al., 2011). Such a seasonal effect could a solution variations in the extent of the gas hydrate stability zone (GHSZ) on the  $Sv<sup>th</sup>$  and margin and the distribution of gas flares in the water column (Ferre et al.,  $2020$ ; Riedel et al., 2018), but the net methane budget still needs to be estimated.  $A_i$  and from seasonal shifting, meteorological events such as storms (Shakhova et al.,  $20<sub>1</sub>$ <sup>4</sup>), chemical gradients and geological sitespecific parameters (Ryerson et al.,  $2\sqrt{11}$ , Schmale et al., 2010a; Schmale et al., 2010b; Yvon-Lewis et al., 2011; Zhang, 2003) can also facilitate methane transfer from the sea to the atmosphere. ntluenced by environmental factors such 's seasong vertical density gradients in the water colu. nn of ght limit the ascent of methane gas to the sease Thack During winter, the vertical mixing in the water colu. The color

As mentioned in section 4.ii, the methane injected in seawater is then submitted to dissolution, gas exchange within the bubbles and oxidation. Modeling of gas bubble ascent can predict the evolution of bubble sizes and the fractions of methane gas reaching the sea surface, and then transferred to the atmosphere under idealized conditions (McGinnis  $\sim$  al., 2006; Ruppel and Kessler, 2017). For a water depth of 100m, methane from only bubbles with a diameter larger than 2cm at the seafloor can reach the atmosphere (Ruppel and Kessler, 2017). Furthermore, the internal dynamics of large-scale bubble plumes and the interactions with ambient bottom currents and density stratification adds further complexity that is not yet fully resolved by numerical models (Leifer et al., 2015; Schneider von Deimling et al., 2015). Such an achievement necessarily requires a sound knowledge, not only of its micro-biological state of the local water column, but also its the physical properties (*i.e.* currents, temperature). Hence, hydro-acoustic measurements and more additional field data are required to monitor and forecast the fate of methane gas released at the seabed to improve the existing models. Thus, in order to reliably evaluate methane contribution from hydrate decomposition to the global atmospheric budget, it is necessary to (1) develop new biogeochemical tools to better identify and decipher all oceanic sources and understand the processes that degrade this molecule in the water column, and (2) intensify observations and monitoring of sites by increasing the number of devoted cruises as well as the deployment of autonomous or remotely operated systems to achieve reliable estimates

of the methane fluxes across the interfaces sediment (geosphere)/ seawater (hydrosphere)/ atmosphere.

Once reaching the uppermost water layer, the diffusive transfer to the atmosphere is strongly affected by ocean state and weather conditions (James et al., 2016; Wanninkhof et al., 2009). Wind speed modifies the exchange velocity across the interface. Wave breaking further enhances gas exchange through bubble formation. Strong winds during storms combine effects of increased water column vertical mixing and gas exchange. At the high latitudes, sea ice acts as a barrier preventing the transfer of methane to the atmosphere (Kort et al., 2012), and accordingly the reduction in sea ice is expected to significantly increase the annual total methane flux to the atmosphere (He et al., 2013). Currently, attempts to accurately measure atmospheric methane inputs from NGHDs, especially in the Arctic where hydrate-bearing sediments are encountered at shallow locations, failed due to widely varying numbers of factors that need to be considered. Using a diffusive model (Wanninkhof, 1992), Thornton et al.,  $(2016)$  estimated a maximum flux range of 68-87 mmol.m<sup>-2</sup>.yr<sup>-1</sup> in the Lapev Sea and East Siberian Arctic Shelf. Comparably, using inverse modelling of atmospheric measurements Myhre et al. (2016) found a source not higher than 120 mmol. $r<sub>u</sub>^{-2}$ ,  $yr<sup>-1</sup>$  off the coast of Svalbard on a known methane seep area (Myhre et al., 2016). When including the impact of storm, Shakhova et al. (2014) proposed higher annual average estimate reaching up to 506 mmol.m<sup>-2</sup>.yr<sup>-1</sup> for the East Siberian Arctic  $\text{Shc}^1$ . For the same area, Berchet et al. (2016) used an atmospheric inversion method  $\pi \dot{\mathcal{A}}$  propose that atmospheric observations in the Arctic are compatible with a mean source ranging between 0-134 mmol.m<sup>-2</sup>.yr<sup>-1</sup>. e Arctic where hydrate-bearing sediments are end<br>due to widely varying numbers of factors th.' ne<br>ve model (Wanninkhof, 1992), Thornto  $\cdot$  et al.,<br>ange of 68-87 mmol.m<sup>2</sup>.yr<sup>1</sup> in the La<sub>I</sub> ev Sea and<br>bly, using inverse

The estimates are different from each other from one site to another as well as from one method to another for the same site, and such a result indicates that several challenges still remain for a better quantification of these fluxes at the sea-air interface. Indeed, the aforementioned studies assumed an atmospheric diffusive flux and estimated it through the gradient method, which does not represent adequately ebullitive fluxes. Atmospheric inversions as top-down methods are unable to unambiguously quantify specifically methane  $r^{-1}$ <sup>2</sup><sub>3</sub><sub>2</sub> from hydrate dissociation distinctly from that originating from other marine out ces. They are further limited by model transport error, embedded sources and atmospheric data coverage. However, top-down methods may provide valuable upper constraints to marine emissions (Berchet et al., 2016). Estimates from closed chamber accumulation could be more accurate but is restricted to a very small spatial coverage, weakening the spatial representativity and therefore remain difficult to operate in open ocean and large areas. The eddy covariance technique deployed on ships is technically adequate (Thornton et al., 2020) but challenging in marine environment, especially because it requires a careful correction of the measured high-frequency, three-dimensional wind for ship motion and attitude (Edson et al., 1998). Measurements are also needed to characterize the sub-seafloor origin of methane, and ground-checked on whether or not it has been buffered in hydrates.

## **5. Strategy to tackle environmental challenges related to hydrate decomposition**

In the previous sections, we have shown the scarcity of methane flux measurements at hydrate-bearing sites and the need to intensify such measurement campaigns. We also stressed the need to undertake investigations at different spatial and temporal scales to gain insights into the impacts of hydrate decomposition on the seafloor stability and the fate of the permafrost. The outcomes of such studies will help to clarify the evolution path of NGHDs and its impact upon climate change or/ and human activity, and how this evolution path affects the ecosystems colonizing the sediment as well as the water column. Addressing the aforementioned environmental challenges requires both the definition of an environmentally sound monitoring strategy and the assessment of the legal framework regulating the release of gases and particles in the water column. The current legal framework must be adjusted to account for the specific environmental risks associated with natural gas hydrate dynamics. Therefore, the following actions should be considered:

- Assess how slope stability may be compromised by either global warming or gas production from hydrates under different geological boundary conditions;
- Identify suitable precursors/changes for slope failure to be targeted in monitoring program;
- Develop a generic strategy for enviror integral baseline studies and the environmental monitoring of hazards  $r^{-1}$  and to gas hydrate dynamics;
- Evaluate whether national and international legal frameworks are suitable to protect the environment.

In the previous sections, the hazards related to gas hydrate decomposition have been identified and discussed, whereas <sup>th</sup>is section is devoted to the risk analysis related to hydrate decomposition. Risk analysis is essential to ensure safety of operations. Although the terms "risk" and "hazard" are often used interchangeably, "risk" and "hazard" have well define.<sup>1</sup> meanings in risk assessment procedure. Hazard is a potential source of harm or damage. Harm or damage is always the consequence of an accident, whereas risk is  $\gamma$  combination of the likelihood (L) of the harm occurring and the severity of that  $h^2$   $\Delta$  (damage D). Thus, risk can be formulated as follows: natural gas hydrate dynamics. Therefore, the follow slope stability may be compromised by eith ar glob from hydrates under different geological boundas suitable precursors/changes for soperalling program; a generic strate

$$
R = f(D, L) = D x L
$$

Where R represents the risk matrix.

### **a. Generic strategy related to gas production from NGHDs**

The production of gas hydrates, whether or not coupled with carbon dioxide sequestration, can create environmental hazards by affecting seafloor stability and delicate microbial/benthic ecosystems and by releasing methane and particles into the water column. Therefore, countries that are considering such resources are committed to developing an appropriately focused environmental baseline survey prior to gas hydrate production operations to quantify those risks. An environmental risk assessment of gas

hydrate exploration and production (E&P) operations will be generated from the baseline survey and will include proposed mitigation measures to minimize the impacts of the E&P operations. During E&P operations, an appropriate monitoring program to assess the effectiveness of mitigation measures is necessary. There are precedents for baseline and monitoring studies from oil and gas E&P (IOGP, October 2017) and  $CO<sub>2</sub>$ storage (https://www.quintessa.org/case-studies/coupled-process-modelling-for-co2 storage).

A lightweight drillship using coiled tubing drilling over a short period of time may be used in NGHD exploration because the NGHD prospect will be at shallow depths in unconsolidated marine sediments. Production of NGHD is likely to be carried out by subsea infrastructure on the seafloor with real-time monitoring and control from a remote location (Max and Johnson, 2019). Hydrate is stable and effectively inert in its reservoir host sediment. During depressurization, which seems the most promising method of production, pressure in the reservoir is lower  $\pm a_{11}$  normal formation pressure which means that a blow-out is physically impossible and the likelihood of leakage of gas is highly reduced. If gas leakage does occur methane gas bubbles are dissolved in ambient seawater during their ascent through the vater column and oxidized by aerobic microorganisms using dissolved oxygen as terminal exectron acceptor (Atlas and Hazen, 2011) with the potential consequences of  $\langle x \rangle$ gen depletion in the water column as detailed in section 4.ii.

Prior to drilling an NGHD exploration borehole, a site survey to establish baseline environmental conditions and identify drilling hazards at the proposed drill site is needed. Site surveys are performed to minimize the risk of harm to personnel and equipment, and to protect the natural environment. Therefore, the site survey must acquire sufficient data over  $\lambda_1$  appropriate period of time to adequately describe the physical, chemical, geological and biological environments in the operational area. Initially a desktop study is carried out to inform the design of the site survey. With respect to the specific hazards presented by NGHDs the integrated analysis of exploration 3D and  $\sim$  2D seismic data, offset well data (logs, operation reports, industry databases, etc.), geotechnical borehole information, offset site surveys and relevant public domain data will allow an initial ground model of the seabed and shallow section to be developed. This geological characterization will include detailed bathymetry, geochemical, mineralogical and petrophysical characteristics of the sediment and geological structures. The biogeochemical characteristics of the seafloor and its surroundings (bottom water, near seafloor sediment characteristics as well as pore water composition, together with the dissolved benthic fluxes) must be measured. Further measurements will be required to establish baseline environmental conditions. These include the physical and chemical characteristics of the entire water column especially in relation to oxygenation and acidification, *i.e.* dissolved gases such as  $O_2$ ,  $CO<sub>2</sub>$ , and CH<sub>4</sub> as well as other parameters of the carbonate system (pH, DIC, alkalinity), nutrients,  $SO_4^2$ ,  $H_2S$ ,  $Ca^{2+}$ , and total Hardness. Potential gas emissions from the seafloor into the water column in the target area should be known, and qualitatively and (Max and Johnson, 2019). Hydrate is stable and eediment. During depressurization, which searms action, pressure in the reservoir is lower that a blow-out is physically impossible and the like duced. If gas leakage does oc

quantitatively mapped (Bayrakci et al., 2014; Greinert et al., 2006; Greinert and Nützel, 2004; Jerram et al., 2015; Leblond et al., 2014) as well by appropriate acoustic devices and sensors (*e.g.* single-, split- and multi-beam echo sounder systems, dissolved gas sensors). The biological environment must also be described including the biological community of the seafloor and near seafloor sediments (biocenosis) with reference to conservation of protected areas, habitats and species. Economic activity that might be impacted by NGHD production operations should be described including archaeological heritage.

The desktop study will confirm if the shallow geology and the environmental hazards generated by the production of gas hydrates is well understood. Invariably supplemental data acquisition will be required, and a site survey will be designed to fill the data gaps identified by the desktop study. Because NGHD E&P operations will involve deploying a seabed coring tool from a workboat, a seabed clearance survey will be required. An indicative site survey area is 200 m below seabed and  $5^{\circ}$  t<sub>hra</sub>dius around the borehole site location.

The baseline studies can be carried out by an autonomous underwater vehicles (AUV) and a seafloor and water column generic instrument module or lander deployed from a site survey vessel with seabed sampling equipment and a towed magnetometer (cf. Klar, 2019 for information on monitoring technology). The seabed sampling using box cores and piston cores deployed from the site curvey vessel will acquire geotechnical information on the strength of near sabed sediments and biological habitats. The magnetometers will provide archaeological information. The AUV and lander should be equipped with suitable instruments to monitor the water column, the water-sediment interface and partially the sub-se<sup> $f$ </sup>oor as well (*e.g.* side scan sonar and synthetic aperture sonars (SAS), echo sounders, sub-bottom profilers, hydrophones, physical sensors, chemical sensors, st<sup>1</sup>l camera, sediment traps, benthic chambers, etc.). It may be necessary to deploy  $\ell$ n au pnomous, fully instrumented lander for several months at the proposed site to  $\partial \mathcal{L}_{\mu}$  ire adequate baseline data and capture variabilities related to season, tide, storm  $x^T C^T$  aforementioned environmental and anthropogenic events. desktop study. Because NGHD E&P operations where<br>desktop study. Because NGHD E&P operations where<br>tool from a workboat, a seabed clearance su, vey<br>prvey area is 200 m below seabed and 500 m, adius<br>adies can be carried out

Geological characterization is necessary to assess the risk and likely impacts of seafloor deformation caused by NGHD E&P operations. The geological characterization will include the aforementioned of surveys and analyses proposed for the site surveys, together with data from OBS (Ocean-Botton Seismometer) or OBC (Ocean-Botton Cable), as well as high-resolution multibeam bathymetry/backscatter mapping of the seabed and hydro-acoustic imaging of shallow gas accumulations in the seabed it they are not already available from site surveys. A paleo-geological history study will also be required. The combination of multibeam backscatter data with the results of the analyses of box cores will allow the characterization of the benthic biotopes of the operational area.

Likewise, to assess the likely impacts of methane gas release on the environment, several parameters will need to be measured in the baseline site survey. In addition to all

aforementioned measurements, these include detection and quantification of gas bubbles in the water column through acoustic systems; sampling and analyses, including both isotopic and molecular composition determination of any ascending gases; video/photo imaging of biota at the seabed; biological integrity; oceanographic measurements to model the transport of sediments and gases; chemical detection of dissolved gases; chemical and isotopic compositions of key pore-water elements and dissolved gases; habitat mapping. Several of these measurements can be achieved by deploying an autonomous seafloor and water column generic instrument module, water column moorings and/ or lander from the site survey vessel to collect the data. However, although some gas (*e.g.* methane, carbon dioxide) sensors can be implemented on these platforms, most of the geochemical analyses of the gas bubbles and pore water will be performed onshore after sampling with appropriate tools such as corer and bubble sampler (Chen et al., 2007; Ruffine et al., 2018a; Ruffine et al., 2018b; Wu et al., 2013; Wu et al., 2014).

The environmental impact assessment will also need to assess the impact of NGHD E&P operations on human economic activity. Therefore, the site survey will also need to acquire information on the physical infrastructures, pipelines, telecommunication cables, fishing activity, etc., in the vicinity of the NGHD E&P operation area. A stakeholder engagement plan may also be n $\infty$ s ary based on the human activity that may be impacted.

With respect to the environmental  $m\tilde{C}$  itering plan for long-term NGHD production operations, it is advisable to deploy an instrumented lander and/ water column moorings to monitor essential environment  $\vec{u}$  variables at an undisturbed reference site within a suitable distance from production operations where a similar lander/ and or water column moorings acquires in ormation on the same essential environmental variables for comparison (Klar et al., 2019). The results of the baseline study based on the site survey data will form the input for modelling (geotechnical, geochemical, fluid flow, etc.) to predict respectively conditions during production and to compare after decommissioning. In addition, the modelling can be used as a tool to plan the monitoring regime and to define the area that may be influenced both temporarily and spatially by the NGHD production. The modelling can help to understand if an additional dataset is necessary to complete the baseline study. Commercial software is only available for partially modelling site evolution, so one suggestion would be to evaluate the possibility to develop new software to enable complete modelling of site evolution. ore after sampling with appropriate tools such a<br>
text al., 2007; Ruffine et al., 2018a; Ruffine et al., 20<br>
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### **b. Generic strategy to monitor gas seepages from hydrates**

After the baseline study has delivered the comprehensive characterization of the site, monitoring is necessary in order to identify any anomalies relative to the anthropic- (*e.g.* pre-production state) or the climate change-related impacts (Liu et al., 2019). Indeed, the strategy detailed in this section applied for assessing the impacts of disturbances due to both human activities and climate change. However, as mentioned previously the

impacts due to climate change may be smoother and expand over a longer time period. Thus, the monitoring period should be adapted accordingly.

The first step towards a suitable monitoring strategy is to generate a detailed project description based on the baseline study and modelling, in order to identify the main risks for the environment and assess the potential impacts. From the environmental impact assessment, a recommendation of mitigation measures and a plan for environmental management and spatiotemporal monitoring should be established. The next step is to plan the management and monitoring strategy based on the risk and impact assessment. Surveys carried out during the baseline study should be repeated. It could include autonomous underwater vehicles (AUVs), monitoring vessels, water column moorings and lander deployments, as used for the baseline study (Klar et al., 2019). Multiple surveys should be conducted for full areal coverage. However, each survey should be conducted at a specific height above the search along with permanent monitoring on and of the seabed by fixed installations such as observation wells and deployed sensors, to achieve optimal results. Additional targeted studies will have to be conducted, if active formation water seeps, gas seens, reological features such as mud volcano and pockmarks, etc., connected to the NGHD producing reservoir are observed at the seabed. These sites must be revisited on  $\lambda$  regular basis to determine emission rates of gases and fluids. Such periodic vi it, are key to check for instance, if any seepage has strengthened and/or seafloor geological structure formation is (re-)activated by the NGHD production operation. It new seeps develop during the production operational phase, they must be investigated and sampled in detail to determine the origin and chemical composition  $\sigma$  the seeping fluids and gases and their emission rates. surveys should be conducted for full area. "over<br>e conducted at a specific height above the 'eau 'ad, a<br>md of the seabed by fixed installations  $2^n$ , as ol<br>s, to achieve optimal results. Additior a. targeted st<br>tive forma

Especially during the NGHE production it is also important to accurately monitor seabed deformation, since  $\alpha$  formation and subsidence processes around the center of activity could already be an imminent hazard precursor. This type of monitoring relies on lander-deployed 'ag' precision, high stability pressure sensors together with inclination measurements at several positions within the production field. Acoustic Long Baseline (LBL) r lethodology can be used to monitor relative positions in between the measuring nodes at the seafloor (Klar et al., 2019).

### **CONCLUSION AND PERSPECTIVES**

Natural gas hydrates have been investigated for multiples purposes for decades, whether to understand their role in the oceanic methane (carbon) cycle, as a geohazard, or as a potential energy resource. Whatever the purpose of their study, the question of their decomposition, -the main factors that trigger this process, its speed and duration, as well as the methane flux released-, are highly relevant. In the present review, the environmental impacts related to hydrate decomposition have been discussed and

monitoring strategies have been proposed to identify and better characterize those impacts.

Hydrate decomposition can be relatively fast, from a few months/ years to few decades, if it is voluntarily caused by human activities. On the other hand, the changing climate of our planet may also trigger the decomposition of vulnerable NGHDs located in the permafrost and the shallow sediments on the ocean margins. The kinetics of such a decomposition will likely be slower but will last over a longer time period. There are natural biogeochemical processes that degrade methane within both the sediment and the water column, preventing any large accumulation of it in the water masses and mitigating its transfer to the atmosphere. However, the question of the efficiency of these processes under a changing climate needs to be understood. How will the increase of sea bottom temperature affect the microbial communities that perform the aerobic and anaerobic oxidation of methane, and accordingly the amount of methane that will be released from hydrates? What will be the consequences of such releases over decades and centuries? These questions remain to be answered.

Coastal regions are amongst the most populated areas on Earth. The decomposition of hydrates, mainly due to climate change, may reduce seafloor stability and cause submarine landslides with associated tsunaming impacting coastal communities. The potential occurrence of such catastrophic socio-economic events that threaten human life, natural resources and key infrastructure in populated coastal regions highlight the need to monitor the dynamics of NGH<sub>2</sub>. This review has shown that field observations and measurements are limited in space and time. Field observations are crucial to achieving an in-depth and comprehensive understanding of the operating environment, and to developing an appropriate environmental monitoring and management plan. Currently, what we observe  $C_1$  a given site is not representative for other sites and an intensification of the measurements of key parameters, both spatially and temporally, is urgently needed. emperature affect the microbial communitie that<br>vidation of methane, and accordingly the a nou it of<br>ydrates? What will be the consequence  $\gamma_0$  such re<br>hese questions remain to be answered<br>are amongst the most populated

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#### **Declaration of interests**

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