Earth and Planetary Science Letters 502 (2018) 1–11

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Investigating a gas hydrate system in apparent disequilibrium in the Danube Fan, Black Sea

Jess I.T. Hillman [a,*], Ewa Burwicz [a], Timo Zander [a], Joerg Bialas [a], Ingo Klaucke [a], Howard Feldman [b], Tina Drexler [b], David Awwiller [b]

[a] *GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany*
[b] *ExxonMobil Upstream Research Company, Houston, TX, USA*

ARTICLE INFO

Article history:
Received 22 March 2018
Received in revised form 21 August 2018
Accepted 23 August 2018
Available online xxxx
Editor: J.-P. Avouac

Keywords:
gas hydrate
modelling
Danube Fan
BSR

ABSTRACT

The Danube Fan in the western Black Sea shows many features indicating the presence of gas and gas hydrates, including a bottom simulating reflection (BSR), high-amplitude anomalies beneath the BSR and the presence of gas flares at the seafloor. The BSR depth derived from 3D P-cable seismic data of an older slope canyon of the fan (the S2 canyon) suggests that the BSR is not in equilibrium with the present-day topography. The Danube Fan was abandoned ∼7.5 ka, and the S2 canyon was likely incised ∼20 ka, suggesting that the gas hydrate system has had at least 7.5 ka years to equilibrate to the present-day conditions.

Here we examine the extent and position of the hydrate stability zone through constructing both steady and transient state models of a 2D profile across the S2 canyon. This was done using inputs from mapping of the 3D P-cable seismic data and geochemical analysis of core samples. Using these models, we investigate the effects of different factors including variable thermal properties of heterogeneous sediments in the vicinity of the canyon and, topographic focusing on the geothermal gradient on the extent of the hydrate stability zone. Our results indicate that both factors have a significant effect and that the hydrate system may actually be in, or approaching equilibrium.

1. Introduction

The observation of a bottom simulating reflection (BSR) in seismic data is generally considered a good indicator for the presence of gas hydrates (Shipley et al., 1979). BSRs are defined in seismic data as reflections that are sub-parallel to the seafloor, cross-cut dipping strata, and in the case of hydrate related BSRs, are opposite in polarity to the seafloor reflection (Boswell et al., 2016; Clennell et al., 1999). BSRs are most frequently interpreted as the result of a negative impedance contrast caused by the transition from gas hydrate bearing sediments above the base of gas hydrate stability (BGHS), to free gas accumulating below the BGHS (Haacke et al., 2007). As data from samples acquired in this area of the Black Sea indicate a gas composition of >99% biogenic methane (Popescu et al., 2006; Zander et al., 2017), we focus on Structure I hydrates, and as such refer to the base of Structure I hydrate stability (BS_IGHS), following the nomenclature of Boswell et al. (2016). Several factors affect the stability of hydrates in marine sediments and consequently the position of the BS_IGHS. The two primary factors are pressure and temperature, as hydrates are only stable at low temperatures and high pressures (Fig. 1) (Clennell et al., 1999; Liu and Flemings, 2011). Other factors include gas composition, porewater salinity, pore size, permeability, capillary forces and grain surface effects (Liu and Flemings, 2011; Xu and Ruppel, 1999). In addition, hydrate can only accumulate where the mass fraction of methane exceeds local methane solubility. Hydrate formation therefore depends on methane flux rate, the solubility of methane and localised conditions of grain-scale saturation, porosity and permeability (Xu and Ruppel, 1999). However, thermal properties of the sediment are also one of the major drivers for the response of the BS_IGHS.

Although this is the subject of some debate, it is generally accepted that the position of the BSR is a reasonable first approximation for the BS_IGHS (Clennell et al., 1999; Riedel and Collett, 2017 and references therein). As temperature is one of the key controls on the occurrence of hydrates, the BSR essentially represents an isotherm related to seafloor depth (Shankar and Riedel, 2010). As a result, the position of the BSR has been used to estimate geothermal gradients and derive information

---

[*] Corresponding author. Now at: GNS Science, 1 Fairway Drive, Avalon 5010, New Zealand.
E-mail address: j.hillman@gns.cri.nz (J.I.T. Hillman).

https://doi.org/10.1016/j.epsl.2018.08.051

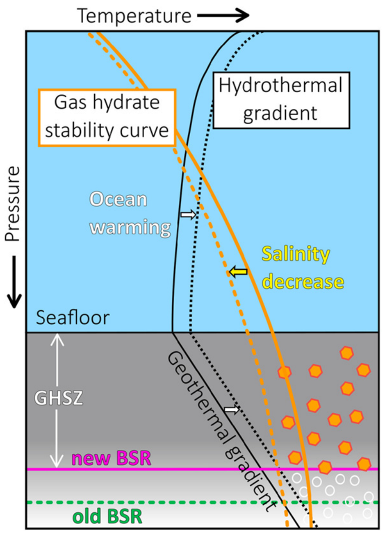

Fig. 1. Gas hydrate stability curve to demonstrate the impact on the gas hydrate stability zone of variations in ocean temperature and salinity. An increase in BWT of 1 °C would shift the base of gas hydrate stability (BS$_{\mathrm{I}}$GHS) upwards. Conversely, an increase in salinity would result in a deepening of the BS$_{\mathrm{I}}$GHS from position A to position B (green dotted line). Filled hexagons indicate gas hydrate in sediments, and open circles represent free gas. After Zander et al. (2017). (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

regarding local conductive heatflow (Shankar and Riedel, 2010; Townend, 1997). In order to estimate geothermal gradients based on the position of the BSR, one must assume a linear temperature gradient, a hydrostatic pressure regime, and, most importantly, that the hydrate system is in equilibrium (Horozal et al., 2017; Shankar and Riedel, 2010; Townend, 1997). Whether the latter is true and how long it takes for the hydrate system to regain equilibrium after a major perturbation is difficult to establish. The response rate of the BS$_{\mathrm{I}}$GHS to different perturbations – such as temperature increase, sea-level rise, sediment deposition – will differ depending on the magnitude of the perturbation and the physical properties of the hydrate-bearing sediment (Reagan and Moridis, 2008). Changes in sea level and sediment deposition events will have a more immediate impact than variations in seawater temperature, as the temperature change needs time before reaching the depth of the BS$_{\mathrm{I}}$GHS. This depends on the thermal properties of the sediment (Reagan and Moridis, 2008; Xu et al., 2001).

Here we investigate the factors that influence and control gas hydrate stability in the northwest Black Sea, with particular focus on a submarine canyon (the S2 canyon) in the Danube Fan. Through observations in 3D seismic data we demonstrate that the hydrate system does not appear to be in equilibrium with present-day seafloor topography. Using 2D and 3D hydrate stability modelling we examine possible causes of this apparent disequilibrium, discussing the influence of submarine slope failure, topographic focusing of heatflow and the thermal properties of heterogeneous sediments.

2. Geological setting and previous work

2.1. Hydrates in the Black Sea

The western Black Sea shelf and the Danube Fan experienced several strong sea-level fluctuations and the change from lacustrine to marine conditions since the last glacial maximum (Lericolais et al., 2013, 2011). However, following the onset of sapropel deposition at 7.5 ka, conditions have remained constant (Lericolais et al., 2013). Previous studies have estimated that the Black Sea contains around 96×10^9 kg of methane dissolved in the water column, with an estimated 1–5×10^{12} m^3 of gas hydrates contained in sediments (Poort et al., 2005; Starostenko et al., 2010). The upper limit of the GHSZ in the Black Sea has been calculated as ∼665 m water depth, based on a bottom water temperature (BWT) of 9 °C and a limnic pore water salinity of 3 psu (Riboulot et al., 2017; Zander et al., 2017). Multiple BSRs (Bottom Simulating Reflections) have been documented in several areas of the Danube Fan (Popescu et al., 2006; Zander et al., 2017). Popescu et al. (2006) propose that the paleo-BSRs correlate to former positions of the BS$_{\mathrm{I}}$GHS, corresponding to stable cold climatic episodes in the region. Zander et al. (2017), conclude that the paleo-BSRs are the result of temperature effects due to rapid sedimentation, rather than changes in BWT or sea-level variations. The preservation of the paleo-BSRs is possibly due to the delayed dissociation of hydrates, resulting in small amounts of free gas remaining beneath the paleo-BSRs, allowing such features to be imaged in seismic data. The fact that the paleo-BSRs are not parallel to each other suggests that there may have been several intermittent phases of hydrate formation, potentially related to paleo-seafloors and levee development (Zander et al., 2017), but with minor amounts of free gas remaining at the position of the previous BSR due to insufficient force to drive upward migration, which is enough to form a paleo-BSR.

In addition to widespread BSRs, gas flares have been recorded in >5000 locations in the Black Sea in water depths of 66–2000 m, although it must be noted that many of these are associated with mud volcanoes (Starostenko et al., 2010). Flares mostly occur in water depths of <700 m, which correlates well with the calculated upper limit of the GHSZ in the Danube Fan (∼665 m) (Naudts et al., 2006; Zander et al., 2017). The origins of shallow gas in the Black Sea are not yet well constrained, and previous studies have shown evidence of both thermogenic and biogenic sources; however, geochemical analysis of shallow cores indicates a dominant biogenic source (Poort et al., 2005; Starostenko et al., 2010). Data from gas seeps and sediment cores in the northwest region show that the composition of the gas in this area is >99% biogenic methane and is thought to be sourced from the upper 2 km of the sedimentary sequence (Popescu et al., 2006; Zander et al., 2017).

The Danube Fan lies in the northwest Black Sea, extending ∼150 km downslope of the shelf break (Fig. 2). The fan is characterised by a distributary network of channels that represent different phases in the development of several stacked channel-levee systems (Popescu et al., 2001; Winguth et al., 2000). The Viteaz Canyon, incising the shelf break at a ∼100 m water depth, and its associated channel extending down to the abyssal plain at depths of >2200 m (Popescu et al., 2004; Winguth et al., 2000) is the most recently active channel in the fan complex. At present day the fan is separated from the Danube River mouth by a ∼120-km-wide shelf, and sediment deposited by the river is trapped nearshore with only suspended sediment reaching the distal sea (Popescu et al., 2001; Winguth et al., 2000). During sea-level lowstands, the Danube river extended to the Viteaz Canyon and other canyons (such as the S2 Canyon, Fig. 2) in the fan complex, and deposited sediment beyond the shelf edge (Popescu et al., 2001; Winguth et al., 2000). The upper reaches down to ∼200 m water depth are dominated by erosional processes resulting in canyon incision and submarine slope failures, while the middle to lower reaches are characterised by deposition and aggradation associated with numerous channels across the fan (Popescu et al., 2001; Zander et al., 2017). During sea-level lowstands the Black Sea was isolated from the Mediterranean Sea, shutting down the inflow of dense, salty bottom water and resulting in lacustrine, non-stratified and oxygenated conditions. The lack of stratified water masses in-