ABUNDANCE AND DYNAMICS OF GAS HYDRATES IN SHALLOW DEPOSITS OF A HIGH-FLUX SEEPAGE SITE IN THE EASTERN BLACK SEA

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ABSTRACT

We investigated a high-flux seepage site in the Eastern Black Sea in order to quantify the content of shallow gas hydrates and to elucidate their physico-chemical behavior. Pressure and non-pressure sediment cores, as well as venting gas were collected at the Batumi seep area (BSA) in about 845 m water depth. Sediments represented late glacial to Holocene deposits. In gravity cores, hydrates were absent in top sediments (lithological Unit 1) but abundant below ca. 0.9 mbsf. Here, hydrates occurred as massive aggregates in deeper sections of the Unit 2 and as disseminated pieces in the underlying Unit 3. Gas from the degassing of pressure cores and from hydrates as well as vent gas were dominated by CH4 (>99.9 mol-% of light hydrocarbons, LHC). Enrichments in CH4 and C2H6 accompanied by depletions in C3H8 and C4-isomers in hydrate-associated gas relative to vent gas resulted from molecular fractionation during hydrate precipitation. Volumetric gas/bulk sediment ratios determined by pressure core degassing approached 20.3. CH4 concentrations reflected hydrate saturations of 5.2% in Unit 2 and 21% of pore volume in Unit 3. It is calculated that over the entire BSA covering 0.5 km2 about 11.3 kt of hydrate-bound CH4 exist in shallow sediments. X-ray diffraction showed structure I hydrate to prevail. Stable O isotope ratios of authigenic carbonates signify that hydrate decomposition along with gas discharge into overlying sediments occurs episodically. From the rough seafloor topography and carbonate data we conclude that in situ dissociation and/or upfloating of shallow-buried hydrates are a typical feature of the BSA.

Keywords: gas hydrates, Black Sea, methane, seepage, Batumi seep area, pressure coring, methane-derived carbonates, stable isotopes

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INTRODUCTION

The Black Sea basin comprises the world’s largest reservoir of dissolved methane ($9.6 \times 10^4$ kt [1]), which is primarily supplied from seeps and decomposing hydrates [2]. It is estimated to contain ca. $10^-50*10^3$ km$^3$ of hydrate-bound methane [3]. So far, numerous hydrocarbon seepage sites fueled from reservoirs in the deeper subsurface were discovered mainly above the upper boundary of the gas hydrate stability zone (GHSZ), which for pure methane hydrates (structure I, sI) is located at about 710 to 720 m water depth [4-5]. In addition, distinct areas of intense hydrocarbon seepage within the GHSZ and associated with shallow hydrates were recognized in recent years (e.g. [6] for refs.).

Especially shallow-buried hydrates are sensitive to changes in the environmental conditions controlling hydrate stability (i.e. temperature, pore water salinity, hydrocarbon availability, hydrostatic pressure; e.g. [7]) compared to their deeply buried counterparts. In the case one or more of these factors change, submarine hydrates might dissociate and release significant amounts of light hydrocarbons (LHC) to the hydrosphere with consequences for the seafloor topography, biogeochemical carbon cycling, and global climate. However, information on total methane amounts trapped in hydrates at individual seepage sites in the Black Sea is sparse. This is mainly due to the technical effort required to determine true gas and hydrate concentrations (i.e. pressure sampling techniques [5, 8]) in deep sea sediments.

In sediments overlying hydrates the anaerobic oxidation of methane (AOM) typically takes place and affects the vertical hydrate distribution. The AOM is mediated by a consortium of methanotrophic archaea and sulfate-reducing bacteria in a transition zone where methane ascending towards the seabed and seawater-derived sulfate meet. Authigenic methane-derived carbonates, formed as by-products of the AOM, might be used as archives of biogeochemical processes since they preserve the geochemical signature of the interstitial water and therefore reflect varying methane seepage activity and hydrate decomposition (e.g. [9-11]). However, authigenic carbonates from deep sea hydrocarbon seep site in the Black Sea have rarely been used to evaluate the long-term stability of associated hydrates, so far [12]. An aspect of particular interest is whether hydrate-derived methane is released constantly over time or mostly in form of huge bursts rapidly exhausting the hydrate reservoir. An improved understanding of processes affecting hydrate formation and dissociation in the past will contribute to a refined prediction of similar processes in the future if global warming leads to an increase of deep water temperatures.

In this study we present total amounts of hydrate-bound methane contained in surface sediments of a highly active hydrocarbon seepage area, the Batumi seep area, in the Eastern Black Sea. Moreover, we discuss the stability of hydrates associated to this seepage site in the past. For the study presented here, we analyzed pressurized and non-pressurized sediment cores as well as authigenic methane-derived carbonates using several state-of-the-art techniques.

SITE DESCRIPTION

Compressional deformation caused by the northward movement of the Arabian plate and westward movement of the Anatolian Block created a W-E trending system of canyons and ridges of diapirc origin on the continental slope off Georgia in the southeastern Black Sea (Fig. 1a; [13-15]).

Our study area, the Batumi seep area (BSA), is located at about 850 m below sealevel in the permanently anoxic Black Sea water body on top of one of such ridges [13]. The BSA is located within the GHSZ for sI hydrate (Fig. 2; [5]) and covers a seafloor area of approx. 0.5 km$^2$ [13]. This area comprises several sites of focused expulsion of bubble-forming free gas [16], which are related to fluid migration along faults fed by reservoirs beneath the base of the GHSZ (BGHSZ) [17]. A bottom simulating reflector–like structure suggested that the BGHSZ is positioned at about 150 m below seafloor (bsf; [17]).
Figure 2: Phase boundaries of the GHSZ calculated for hydrate structure I at the BSA (modified after [5]). For illustration, a geothermal gradient of 26 mK m⁻¹ reported for that region [18] was used.

The presence of shallow hydrates at the BSA was inferred from high seafloor backscatter intensities and seismic profiles [13, 17], and was evidenced by the recovery of hydrate pieces [5, 13]. Vigorous gas bubble discharge into bottom waters was recognized during five cruises from 2004 to 2011 (Table 1) suggesting sustained gas flux towards the seafloor sufficient to maintain hydrates in the shallow subsurface. In addition, a rough local seafloor topography was observed during ROV-based video documented.

Table 1. Specifics of expeditions dedicated for the exploration of the BSA.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Research Vessel</th>
<th>Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>POS 317/4</td>
<td>POSEIDON</td>
<td>10 – 11/2004</td>
</tr>
<tr>
<td>TTR-15</td>
<td>PROFESSOR LOGACHEV</td>
<td>06 – 07/2005</td>
</tr>
<tr>
<td>M72/3</td>
<td>METEOR</td>
<td>03 – 04/2007</td>
</tr>
<tr>
<td>MSM15/2</td>
<td>MARIA S. MERIAN</td>
<td>05 – 06/2010</td>
</tr>
<tr>
<td>M84/2</td>
<td>METEOR</td>
<td>02 – 04/2011</td>
</tr>
</tbody>
</table>

In 2007, gas flares rising up to about 300 m below sea level were observed and a maximum gas flux of 5.5 L min⁻¹ from single outlets was calculated [16]. Moreover, based on observations in 2005 an annual flux of dissolved methane of 2.45 * 10⁶ mol was calculated for a field covering 0.31 km² of the BSA [19]. From the gas molecular composition and stable carbon and hydrogen isotopic composition of methane collected from different sites at the BSA, a mixture of light hydrocarbons of thermogenic origin and from biogenic sources was inferred [5]. Visual examinations by use of ROVs revealed that carbonate pavements are widespread at the seepage sites.

METHODS

Five research cruises from fall 2004 to spring 2011 were conducted to the BSA so far (Table 1). During cruises TTR-15, M72/3, and MSM15/2 seafloor inspections and precise samplings could have been performed by use of remotely operated vehicles (ROVs).

Sampling

During M72/3, non-pressurized sediment cores were taken for sediment sampling and for the collection of hydrate pieces with a gravity corer (GC) equipped with a 6 m core cutting barrel. Hydrate pieces were extracted from the cores immediately upon recovery and either transferred into liquid nitrogen (−196°C) for long-term storage and analysis onshore or for dissociation at room temperature and onboard analysis of hydrate-bound volatiles.

Vent gas forming bubbles in the water column was collected several centimeters above the seafloor with the Gas Bubble Sampler (GBS; [5]) operated by the ROV ‘QUEST 4000m’ during M72/3. For quantification of gas in near-surface sediments, sediment cores were sampled under in situ hydrostatic pressure with the Dynamic Autoclave Piston Corer (DAPC; [5, 20-21]). The DAPC consists of a gas-tight pressure chamber and a core cutting barrel (2.65 m length) with a maximum core volume of ~14 L. Gas contained in the pressure chamber was released incrementally via an assembly of gas-tight valves and ports for gas quantification and gas sub-sampling for molecular analysis.

Pieces of authigenic carbonates retrieved during TTR-15 cruise with a TV-guided grab from station BS377GR (Fig. 1b) were cut into sub-samples and prepared for mineralogical analyses by X-ray diffractometry (XRD).

Analysis

Molecular compositions of gas samples (i.e. sedimentary gas from pressure cores, vent gas, and hydrate-bound gas) were analyzed onboard with a two-channel gas chromatograph [5]. Quantitative phase analyses of hydrate pieces recovered from several GC stations (Fig. 1b) were done by X-ray diffraction [22-23]. Hydrate phase boundaries were calculated for hydrate sI using the CSMGem software package [7] and Heriot-Watt-Hydrate software [24] using gas molecular compositions and average interstitial water salini-
ties for late glacial to Holocene deposits. Bottom water temperatures determined during an ROV dive in spring 2007 at the BSA summit were 8.96 °C; LHC and CO2 composition as given in Table 2. Stable oxygen and carbon isotope analyses of carbonate subsamples were done with a Finnigan MAT 251 mass spectrometer [12].

RESULTS AND DISCUSSION

Sedimentology
Gravity cores and pressure cores from the BSA comprised the typical basinal succession of hemipelagic sediments consisting of finely laminated coccolith ooze (Unit 1; [25]) and mid-Holocene sapropel (Unit 2) overlying late Pleistocene-early Holocene lacustrine clayey-silty mud (Unit 3; Fig. 3).

The two uppermost (marine) units were under-represented in some cores (e.g. GC 06, GC 18, DAPC 09, DAPC 14) compared to others or even absent (DAPC 03, 08). Along with the rough local seafloor topography this indicates a highly dynamic sedimentary environment for at least the last 8.0 kyrs [26]. At the carbonate sampling site the sedimentary blanket of Unit 1 was punctuated by numerous cm-sized holes and irregularly-shaped carbonate build-ups giving rise to a highly irregular sea-floor topography.

Hydrate occurrences
If hydrates were present in gravity cores, they were found below Unit 1 sediments, in some cases co-occurring with a partial cementation of the overlying Unit 1 sediments [5, 13]. Shallowest hydrates were present in Unit 2 of GC 18 in about 90 cmbsf (Fig. 3) taken in an area of focused gas expulsion (Fig. 1b). Near-surface hydrates, indicative of high upward methane flux (e.g. [27-28]), were found dispersed in high density in Unit 3 of gravity cores (GC 06, 08, 13 and 23) irrespective of the thicknesses of the overlying sediments.

In GC 04 and 08, which were taken remote from sites of focused seepage, isolated, several cm-thick layers of massive hydrates occurred close to the base of the sapropelic Unit 2 in spatial association with relatively coarse-grained aragonitic interlayers [5].

As for other hydrocarbon seeps, the absence of hydrates in the uppermost deposits of our study area seems to be primarily controlled by the AOM [29] and diffusion into the methane undersaturated bottom water. However, since the overlying Units 1 and 2 are characterized by smaller grain sizes than Unit 3, the accumulation of hydrates in the aragonitic interlayers at the base of Unit 2 and in the clayey-silty Unit 3 might also be attributed to differences in permeability and porosity.

Figure 3: Lithological compositions of pressure cores (DAPC) and non-pressure cores (GC) recovered from the BSA (modified after [5]).
Gas molecular composition
By use of multiple sampling tools, i.e. DAPC, gravity corer, and GBS, gases from different near-surface gas pools (e.g. sedimentary gas, hydrate-bound gas, and venting free gas) could be collected at the BSA. Average hydrocarbon compositions in gases retrieved from these pools were strongly dominated by methane (99.90 to 99.94 mol-% of $\Sigma$(C$_1$−C$_4$, CO$_2$)) followed by ethane (0.02 to 0.04 mol-%; Table 2). Propane, iso- and n-butane were found in much smaller amounts and C$_5$- and C$_6$-derivatives were present only in traces occasionally in vent gas. Carbon dioxide ranged between 0.03 and 0.08 mol-%.

Table 2. Molecular composition (in mol-% of $\Sigma$(C$_1$−C$_4$, CO$_2$)) of gas samples collected from individual pools at the BSA. Note: Gas compositions are mean values calculated for multiple samples (see also [5]).

<table>
<thead>
<tr>
<th></th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>C$_3$</th>
<th>i-C$_4$</th>
<th>n-C$_4$</th>
<th>CO$_2$</th>
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</thead>
<tbody>
<tr>
<td>Sediment</td>
<td>99.931</td>
<td>0.039</td>
<td>0.001</td>
<td>tr.</td>
<td>tr.</td>
<td>0.030</td>
</tr>
<tr>
<td>Hydrate</td>
<td>99.939</td>
<td>0.030</td>
<td>0.001</td>
<td>tr.</td>
<td>tr.</td>
<td>0.029</td>
</tr>
<tr>
<td>Vent</td>
<td>99.902</td>
<td>0.019</td>
<td>0.004</td>
<td>0.001</td>
<td>tr.</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Sediment = Sedimentary gas; Hydrate = hydrate-bound gas; Vent = Vent gas; tr. < 0.0001

In general, hydrate-bound gas was enriched in methane and ethane, depleted in propane and carbon dioxide, and virtually devoid of iso-butane and n-butane relative to vent gas. Similar molecular distinctions observed at different hydrate-bearing sites (e.g. [7, 30-31] were attributed to molecular fractionations due to size exclusion during hydrate crystallization.

Gas inventory
Gas volumes (at atmospheric pressure) determined by controlled degassing of the seven DAPC cores ranged between 3.7 and 20.3 L gas per L wet sediment (Table 3). The highest volumetric gas / sediment ratio was determined for DAPC 08 which was taken close to focused seepage (Fig. 1b) and contained the highest portions of sediment belonging to Unit 3 (Fig. 3). Notably, DAPC 14, taken close to DAPC 08, yielded only 14.1 L gas per L sediment. This might be due to the recovery of less Unit 3 material which in general contained highest proportions of hydrates and, thus, highest gas concentrations (Fig. 3).

By comparing sediment volumes belonging to individual lithological units (1 to 3) in the pressure cores, unit-specific methane concentrations were assigned. The amount of hydrate-bound methane in each pressure core from Units 2 and 3 was computed by subtracting the amount of free gas and that of dissolved methane that would be in equilibrium with hydrate with full occupancy from the total inventory of methane contained in each pressure core.

Table 3. Gas volumes retrieved from pressure cores and calculated volumetric gas to sediment ratios.

<table>
<thead>
<tr>
<th></th>
<th>Core volume</th>
<th>Gas volume</th>
<th>Gas – sediment ratio</th>
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<tbody>
<tr>
<td>#</td>
<td>[L]</td>
<td>[L]</td>
<td>[L L$^{-1}$]</td>
</tr>
<tr>
<td>01</td>
<td>14.1</td>
<td>231.2</td>
<td>16.4</td>
</tr>
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<td>03</td>
<td>4.4</td>
<td>40.7</td>
<td>9.3</td>
</tr>
<tr>
<td>08</td>
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<td>13.8</td>
<td>100.6</td>
<td>7.3</td>
</tr>
<tr>
<td>12</td>
<td>2.2</td>
<td>8.0</td>
<td>3.7</td>
</tr>
<tr>
<td>14</td>
<td>7.3</td>
<td>103.3</td>
<td>14.2</td>
</tr>
<tr>
<td>15</td>
<td>7.8</td>
<td>137.5</td>
<td>17.6</td>
</tr>
</tbody>
</table>

The methane concentration surpassing in situ solubility in Unit 2 and Unit 3 were attributed to hydrates which were found in all gravity cores in depths >90 cmbsf (Fig. 3). Calculations of hydrate volume fractions in pore volumes (pv) of each sediment unit based on the in situ solubility revealed that hydrates filled about 5.2% of pv in Unit 2 and between 9.1%pv (DAPC 03, off area of focused gas ebullition) and 34.2%pv (DAPC 15, within area of focused gas seepage) in Unit 3 (mean 21.0%, n = 5). Hydrate fractions calculated for Unit 3 in our pressure cores are comparable to those reported for sections below the sulfate zone in three pressure cores recovered in 2005 from the BSA [8, 19].

Overall methane masses
Overall masses of methane stored in the sediments and in sI hydrate, which is the stable structure at the BSA [32], were calculated using average thicknesses of Unit 1 (0 to 30 cmbsf) and Unit 2 (30 to 106 cmbsf) deposits and assuming that the remaining sediment recovered belonged to Unit 3 (106 to 265 cmbsf; maximal core recovery). We extrapolate that for the seafloor area characterized by high-backscatter (0.5 km$^2$; 1,172,500 m$^3$) methane in surface sediments would account for 13.3 kt. Methane in shallow hydrates accounts for about 11.3 kt. This mass of hydrate-bound methane at the BSA corresponds to approximately 0.25% of the mass of methane considered to be annually emitted from Black Sea seeps and decomposing hydrates [2].
Gas hydrate dynamics

Because hydrate-bound water is typically enriched in the stable oxygen isotope $^{18}$O relative to pore water, pore water affected by hydrate dissociation is typically enriched by up to 3.3‰ in $^{18}$O [33]. Moreover, the stable oxygen isotope ratio of authigenic seep-associated carbonates incorporating pore water derived oxygen reflects periods of hydrate decomposition (e.g. [9-10]). In order to unravel the role of hydrate decomposition on the formation mechanisms of shallow carbonates at the BSA in the past, authigenic methane-derived carbonates were analyzed for their stable oxygen isotope ratios. The results indicate that high-Mg calcite, which cemented deformed coccolith ooze (max. age 2.7 kyrs [34]), incorporated pore water mixed with substantial hydrate-water amounts ($\delta^{18}$O ~0.8–1.7). The enrichment of $^{18}$O relative to equilibrium conditions (considering temperature and isotopic compositions of bottom water as well as carbonate mineralogy) points at a dominant role of high gas/fluid flux from decomposing hydrates leading to the cementation of the overlying sediment. In contrast, aragonitic carbonate rims (e.g. [12, 35-36] associated with vital AOM-performing microbial mats [37-38] and, thus, probably formed in recent times, are characterized by lower values ($\delta^{18}$O ~0.3–0.7). These $\delta^{18}$O-values are consistent with carbonate precipitation in equilibrium with bottom water conditions and, hence, point to an absence of hydrate-derived water during carbonate formation. The differences in $\delta^{18}$O between the presumably (sub)recent aragonite precipitates and the older high-Mg cements suggest that the different carbonate phases reflect periods of hydrate dissociation and vigorous fluid discharge in overlying sediments (imprinted in the $^{18}$O-enriched high-Mg calcite cements) alternating with times of hydrate build-up stability and moderate fluid flow (aragonite rims). This implies that shallow buried hydrates are prone to episodic in situ decomposition with associated vigorous fluid flow as a transient process.

According to phase calculations, dissociation of the sI hydrates at the BSA would be initiated when the current bottom water temperature is increased by about 1.6 °C (Fig. 2). Given the present-day stable stratification of the Black Sea, bottom water temperature variations exceeding 1.6 °C in amplitude are highly unlikely to have been occurred in the mid to late Holocene. Thus, endogenic mechanisms are likely to have induced hydrate dissociation in the near sub-surface, the most probable being an interruption of the methane supply.

Conclusion

1. During the sampling campaigns at the Batumi seep area (BSA) hydrates occurred in the lowermost late glacial to Holocene units below 90 cmbsf as massive aggregates associated with coarse-grained aragonitic inter-layers in deeper sections of the sapropelic Unit 2, and disseminated throughout the lacustrine mud of Unit 3.

2. Hydrates fuelled by vent gas accumulate in deeper sediment sections due to hydrocarbon supersaturation. Nominal methane concentrations retrieved by pressure coring considerably exceeded in situ solubilities in Units 2 and 3 causing gas hydrate formation in these units.

3. Enrichments in methane and ethane along with depletions in propane and carbon dioxide in sedimentary gas from pressure cores and hydrate-bound gas relative to vent gas signify molecular partitioning during sI hydrate precipitation.

4. The uppermost sediment body in that area (0.5 km² seafloor area; 0 to 265 cmbsf) comprised about 13.3 kt of methane. Calculations of hydrate volumes revealed that hydrates filled about 5.2% of the pore volume in Unit 2 and 21% in Unit 3 corresponding to 11.3 kt of hydrate-bound methane.

5. Short-term changes in P/T-conditions affecting hydrate stability at the BSA are not likely in the near future. This conclusion draws from phase calculations indicating preferential precipitation of hydrate structure sI for which the dissociation temperature is about 1.6 °C higher than actual bottom water temperature.

6. Stable oxygen isotopic signatures point at hydrate dissociation affecting carbonate cementation of the coccolith ooze (max. age 2.7 kyrs). In contrast hydrate decomposition is not substantiated for (sub)recent carbonate precipitates.
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[21] Heeschen KU, Hohnberg HJ, Haeckel M, Abegg F, Drews M, Bohrmann G In situ


APPENDIX

ACKNOWLEDGEMENTS

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