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Quantifying in-situ gas hydrates at active seep sites in the eastern Black Sea using pressure coring technique

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BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

In the eastern Black Sea, we determined methane (CH_4) concentrations, gas hydrate volumes and their vertical distribution from combined gas and chloride (Cl^-) measurements within pressurized sediment cores. The total gas volume collected from the cores corresponds to concentrations of 1.2–1.4 mol of methane per kg porewater at in-situ pressure, which is equivalent to a gas hydrate saturation of 15–18% of pore volume and amongst the highest values detected in shallow seep sediments. At the central seep site, a high-resolution Cl^- profile resolves the upper gas hydrate stability boundary and a continuous layer of hydrates in a sediment column of 120 cm thickness. Including this information, a more precise gas hydrate saturation of 22–24% pore volume can be calculated. This is higher in comparison to a saturation calculated from the Cl^- profile alone, resulting in 14.4%. The likely explanation is an active gas hydrate formation from CH_4 gas ebullition. The hydrocarbons at Batumi Seep are of shallow biogenic origin ($\text{CH}_4 > 99.6\%$), at Pechori Mound they originate from deeper thermo-catalytic processes as indicated by the lower ratios of C_1 to C_2 – C_3 and the presence of C_5 .

1 Introduction

Gas hydrates consist of water cages enclosing methane (CH_4) as the major guest molecule (Sloan and Koh, 2007). Given that pore fluids are saturated with CH_4 , gas hydrates form at high pressure and low temperature conditions common at ocean depths exceeding 300–500 m (Sloan and Koh, 2007). Because of the difficulties to inventory marine gas hydrates, considerable controversy remains about the amount and distribution of gas hydrates in marine sediments, and thus their potential as an energy resource or a contributor to past and future climate changes (e.g., Milkov, 2005).

Inventory uncertainties arise from the loss of gas during core recovery, crude sampling resolution, and/or uncertain calibration of indirect methods such as acoustic

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



detections (Dickens et al., 1997; Milkov, 2005). Porewater chloride (Cl^-) anomalies are frequently used to estimate gas hydrate volumes. This is based on the exclusion of salt from the hydrate crystal lattice during hydrate formation in the sediment and the respective fresh water release when decomposition is initiated during core recovery, resulting in negative Cl^- anomalies where gas hydrates had been present (e.g., Haeckel et al., 2004). However, small scale distributional variations, non-steady state conditions, and brine formation in hydrate voids contribute to estimate uncertainties as do variations of Cl^- caused by the advection of less saline fluids from depth (Haeckel et al., 2004). Pressure cores were developed within the ODP/IODP program (Dickens et al., 1997) and for coring of surface sediments (Abegg et al., 2008; Heeschen et al., 2007). They allow for determining the sediment's total in-situ CH_4 inventory that is present as hydrate-bound, gaseous and dissolved CH_4 . This inventory then allows the calculation of the gas hydrate volume based on stability conditions and the equation of state.

Here we compare gas hydrate inventory estimates using two methods: the collection of gas from pressurized sediment cores and porewater chloride anomalies measured on the same cores. The samples originate from recently discovered seep sites off Georgia in the eastern Black Sea (Akhmetzhanov et al., 2007; Bohrmann et al., 2007). Despite gas hydrate discoveries in this area (Klaucke et al., 2006; Pape et al., 2010) little is known about gas hydrate distributions and regional quantities in the Black Sea, the largest anoxic basin at present times (Ross and Degens, 1974). Our results indicate that the gas hydrate volumes are amongst the highest in seep surface sediments worldwide.

2 Geological setting

The Black Sea is an extensional basin with organic-rich sediments of varying salinity and a total of 12–16 km thickness. This stack includes the thick clay-rich Maikopian Unit (Ross and Degens, 1974), which is the source of frequent mud diapirism (Ross and

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Degens, 1974; Wagner-Friedrichs, 2007). Seep sites with CH₄ gas ebullition and fluid flow are common in the Black Sea basin and lead to very high CH₄ concentration in the anoxic bottom waters (Reeburgh, 2007) and widely distributed gas hydrate occurrences in the sediments (Vassilev and Dimitrov, 2002). Large numbers of gas seeps have also been discovered in the south eastern Black Sea (Klaucke et al., 2006), which is characterized by severe faulting and slumping (Ross and Degens, 1974).

Batumi (water depth: 850 m) and Pechori seeps (1000 m) are located on the Kobuleti Ridge, a complex canyon-ridge system (Fig. 1) where buried diapiric structures and fault systems form migration pathways for sediments, fluids and gases (Wagner-Friedrichs, 2007). The Batumi seep area is the largest seep site with an areal extent of 0.5 km² characterized by shallow gas hydrates, authigenic carbonates, and vigorous gas venting (Klaucke et al., 2006; Pape et al., 2010). Pechori Mound has 75 m of relief, steep slopes, and strong seafloor reflection at the top (Wagner-Friedrichs, 2007). It is rich in oil and massive gas hydrates. Indications for structure I gas hydrate, i.e., gas hydrates with CH₄ as the prevailing guest molecule, were found at both sites (Pape et al., 2010; S. Klapp, Univ. Bremen, personal communication, 2008).

3 Methods

The sediment cores originate from pressure coring operations using the Dynamic Autoclave Piston Corer (DAPC) (Abegg et al., 2008) on board R/V *Logachev* (Akhmetzhanov et al., 2007), cruise TTR-15 (Table 1). The cores were degassed on board and subsequently sampled for porewater fluids.

3.1 Pressure coring, gas collection and volume calculations

The DAPC recovers a sediment core of up to 2.3 m length at in-situ pressure using a newly developed enhanced pressure-preserving system. Once on board, its pressure chamber is fixed upright, cooled in an ice-bath and linked to a pressure sensor,

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



an assembly of gas-tight valves for gas sub-sampling, and a volumetric plastic cylinder that allows the measurement of released water and gas volumes. For details: Heeschen et al. (2007). The main degassing takes several hours and is stopped when gas bubbling has ceased for several tens of minutes. When the core has warmed to ambient temperature, it is reopened to collect the small amounts of residual exsolved gas.

The gas samples were analyzed with an Agilent gas chromatograph for hydrocarbons C_1 – C_5 (FID) and for oxygen, nitrogen and CO_2 (TCD). Standards were: 100% C_1 , C_2 , C_3 and CO_2 , bottled mixtures of 100 ppm and 1000 ppm C_1 through C_5 standards (in nitrogen), and air. The precision of standard measurements was 3%. Contaminations of the core gas with air was measured ($\Sigma O_2 + N_2$; 2–2.5%, Table 2) and subtracted. The hydrocarbon gas compositions are given in percentage of the sum of hydrocarbon gases ($\% \Sigma C_{1-5}$, hereafter cited as %). The accuracy of the total gas volumes (gas L^{-1} ; Table 2) is generally 5%. For details: Heeschen et al. (2007).

All dissolved, free, and hydrate-bound CH_4 (ΣCH_4 , mol) is released and collected from the core during its controlled degassing. To calculate the porewater CH_4 in-situ concentration in mol of CH_4 per kg porewater (Table 2), ΣCH_4 is related to the amount of porewater present between the bottom of the core and the sulfate depletion depth, assuming an even distribution throughout this depth range (Heeschen et al., 2007). Assuming dissolved and hydrate-bound CH_4 to be present, we subtract the saturation concentration (c_{eq}) of $0.087 \text{ mol } CH_4 \text{ kg}^{-1}$ (Tishchenko et al., 2005; also see Appendix A) before calculating gas hydrate volumes. The molar CH_4 /water ratio for the structure I gas hydrates is assumed to be 5.9, a value that was observed in natural structure I gas hydrates with an occupancy of 90% of small cages by CH_4 (Ussler and Paull, 2001). All gas volumes refer to STP conditions (1 bar and $25^\circ C$), resulting in a CH_4 volume of 182 L per liter of gas hydrate.

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.2 Gas hydrate and porewater analysis

The gas hydrates were recovered with TV-grab (TVG) or gravity corer (GC). Clean samples were put into headspace vials that were sealed by crimping, and vented into a second vial by a vacutainer. The gas was analyzed on board (see Sect. 3.1).

The sediment of DAPC cores was sampled for porewater. In case of core BS351AP the entire core was cut into 5 cm thick slices. Porewater was extracted using a low-pressure squeezer (<5 bar; 8 °C; 0.2 µm cellulose acetate Nuclepore filters) and analysed for SO_4^{2-} and Cl^- using ion chromatography and Mohr titration, respectively (Wallmann et al., 2006 and references therein). IAPSO seawater standard was used for calibration. Precision of the Mohr titration is in the range of $\pm 10 \text{ mM Cl}^-$. The porosity listed in Table 1 was determined by weight difference, before and after freeze-drying. For the conversion into volume ratio (volume of porewater/volume of bulk sediment) we apply a dry sediment density of 2.5 g cm^{-3} (Haeckel et al., 2004) and a Black Sea water density of 1.021 g cm^{-3} .

The core depths of BS351AP are corrected for the loss of surface sediments caused by the heavy coring gear using porosity data from video guided multi core sampling at the same geographical coordinates (Table 1, Appendix A).

3.3 Modeling the chloride anomaly for its relation to the hydrate content

Observed Cl^- anomalies can be converted to an amount of gas hydrate in percent of the pore volume (GH, % pv) using:

$$\text{GH} = \frac{\Delta\text{Cl}}{\text{Cl}_{\text{ref}}} \frac{\rho_{\text{PW}}}{\rho_{\text{GH}}} \frac{M_{\text{GH}}}{M_{\text{H}_2\text{O}}} \frac{1}{x_{\text{H}_2\text{O}}} \quad (1)$$

where ΔCl = deviation of measured Cl^- concentration from in-situ value (Cl_{ref}), ρ_{PW} = density of porewater, ρ_{GH} = density of natural hydrate, M_{GH} = molecular weight of methane hydrate, $M_{\text{H}_2\text{O}}$ = molecular weight of water, and $x_{\text{H}_2\text{O}}$ = molar ratio of water/methane for natural gas hydrate (Table A1). A numerical 1-D transport-reaction

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



model (Haeckel et al., 2004) was applied to provide the theoretical in-situ Cl^- concentration profile (Cl_{ref}). See Appendix for details on the model.

4 Results and Discussion

4.1 Highest CH_4 concentrations in shallow anoxic seep sediments

5 Most of the in-situ CH_4 concentrations in shallow sediments of the eastern Black Sea seeps (Table 2) considerably exceed values determined from pressurized cores taken in equivalent environments elsewhere (Heeschen et al., 2007). Maximum gas volumes occurred at sites of very high backscatter intensity at Batumi Seep (BS378AP, 200 L and BS351AP, 226 L) (Fig. 1). The shorter core, BS371AP, was taken slightly to the NE
10 and had a smaller gas volume (11 L). At the central high backscatter zone of Pechori Mound core BS359 contained 88 L.

The large gas volumes from the high reflectivity zones relate to consistent in-situ CH_4 concentrations of 1.2–1.4 mol of methane per kg porewater (from here on: mol $\text{CH}_4 \text{ kg}^{-1}$) at depths below sulfate penetration (Table 2). These CH_4 concentrations are ~30% higher than those of surface seep sediments from the gas hydrate stability zone in the Gulf of Mexico and the Anaximander Mountains (Mediterranean Sea) where maximum in-situ CH_4 concentrations were about 1 mol $\text{CH}_4 \text{ kg}^{-1}$ (Heeschen et al., 2007). Concentrations from conventional and pressurized coring differ by two orders of magnitude at all sites caused by loss of CH_4 during core retrieval. For example,
15 at Batumi Seep, maximum CH_4 concentrations of 0.013 mol $\text{CH}_4 \text{ kg}^{-1}$ were measured in conventional cores (Klaucke et al., 2006). This is despite the visual observations of gas hydrates and a calculated CH_4 saturation (c_{eq}) of 0.087 mol $\text{CH}_4 \text{ kg}^{-1}$ in the presence of gas hydrates at the site.

25 All in-situ CH_4 concentrations are far above saturation. The excess CH_4 ($> c_{\text{eq}}$) is bound in gas hydrate, which at three out of four sites occupies a rather consistent pore volume of ~16.5% (% pv) or a core volume of 12% (% cv) at any depth between the

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sulfate penetration and the core bottom (Table 2, Fig. 2a). For better comparison with published data we refer to % pv hereafter. Core BS371AP from the area of intermediate backscatter intensity still holds 2% pv of gas hydrates.

Despite the low fluid advection rates at Batumi Seep of 0.1 cm a^{-1} (see Appendix A), the gas hydrate volumes are slightly higher than the average of 5–15% pv estimated for high fluid flow sites (Milkov, 2005). It is therefore likely that the strong gas hydrate formation is fueled by the vigorous gas ebullition observed in the area (Klaucke et al., 2006; Pape et al., 2010). This inference further supports earlier calculations (Haacke et al., 2009; Haeckel et al., 2004), requiring free gas transport for the formation of high amounts of near-surface gas hydrates.

4.2 Gas hydrate distribution from chloride measurements

The degassing of DAPC cores holds no information on the vertical distribution of gas hydrates in the sediment as do high-resolution Cl^- profiles commonly used on conventional cores to determine the gas hydrate distribution and quantities. The main argument against the latter application is the assumption of a linear background Cl^- profile, thus potentially ignoring the possibility of local Cl^- enrichments from recent gas hydrate formation (Haeckel et al., 2004) and the presence of brines or free gas in gas hydrate voids (Milkov et al., 2004).

To compare two methods of gas hydrate budgeting and use respective advantages, we established a high-resolution Cl^- profile in the gas-rich core, BS351AP, from Batumi Seep after degassing (Fig. 2b and c). At the seep two processes lower the Cl^- concentration: (1) the upward-directed transport of Cl^- -depleted fluids from deeper limnic sediments (Ross and Degens, 1974) that induces linearly decreasing background Cl^- concentrations with depth and (2) local gas hydrate decomposition, which leads to irregular Cl^- excursions from the baseline. Combining the high-resolution Cl^- profile from BS351AP and 1-D numerical transport-reaction modeling is clearly able to resolve both processes (Fig. 2b and c, Appendix A). Whereas transport processes determine

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the background concentrations (dotted line), the decomposition of gas hydrates leads to a broad diversion (solid line) at 85–205 cm (depth corrected, Table 1) plus comparably small diversions at 75 and 225 cm, both of them within the precision of the Cl^- measurements. Calculations using the major Cl^- anomaly between 85–205 cm core depth result in a mean in-situ CH_4 concentration of $1.04 \text{ mol CH}_4 \text{ kg}^{-1}$ in this depth range. This is equivalent to an average gas hydrate volume of 14.4% pv containing 125 L of CH_4 gas (at STP). Including the possible Cl^- anomalies above and below the interval of 85–205 cm, the total gas volume is 140.7 L, thus indicating that at most 12% of gas may originate from depths beyond 85–205 cm.

From the Cl^- profile it becomes clear that nearly all gas hydrate is present at 85–205 cm. If the CH_4 inventory gained from core degassing is corrected for this true depth range of gas hydrate occurrences, the degassed CH_4 volume relates to an average CH_4 concentration of $1.945 \text{ mol CH}_4 \text{ kg}^{-1}$ and a gas hydrate occupancy of 24% pv in a layer with a thickness of 120 cm (Fig. 2, Table 2: BS351AP^{85–205 cm}). Assuming that a maximum of 12% of collected gas is located at other depths this occupancy relates to 22% pv (Fig. 2, Table 2: BS351AP^{85–205, 88%}). This is 7–10% above the value from Cl^- -based calculations.

The disparity between the methods can be explained by active formation of hydrates and non-steady state conditions producing significant in-situ Cl^- enrichments. These cannot be accounted for with a steady state model, nor can they be resolved in pore-water profiles of retrieved cores as they are overprinted by (a) the freshening due to gas hydrate decomposition during core recovery (and degassing procedure) and (b) dilution due to diffusive and, particularly, advective mixing with the lower chloride concentrations in the surrounding porewater (Haeckel et al., 2004) (Appendix A). It is unlikely that the disparity is caused by the presence of a substantial amount of free gas, i.e. not bound in gas hydrates. During degassing free gas would be released first, while gas hydrates are still stable. It would be enriched in gas molecules excluded from gas hydrate formation or be similar to the advecting vent gas if caused by ebullition. In core BS351AP, only the first 11 L of the released gas have a slightly different

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



gas composition with ethane (C₂) being enriched (Appendix B). However, this volume would only account for 0.5% of the gas hydrate volume, i.e., a small fraction of the disparity.

Our approach of combining both methods provides the means to greatly improve the quantification of sedimentary hydrate contents via pressure coring. While the degassing of pressurized cores resolves quantities and gas compositions, the Cl⁻ profile holds information about the vertical gas hydrate distribution and determines gas hydrate stability conditions (Heeschen et al., 2007; Milkov et al., 2004). Further, a discrepancy between both methods is a good indicator for recent and ongoing gas hydrate formation.

4.3 Gas compositions derived from pressure coring

The composition of the gas released from the DAPC cores consists of hydrocarbons (98%) and small contaminations of air of 2–2.5% (Table 2), which we subtracted. At Batumi Seep the released hydrocarbons ($\Sigma_{C_1-C_5}$) consist of 99.63% CH₄, a small contribution of ethane, and traces of propane, whereas at Pechori Mound C₂ and C₃ compositions are one order of magnitude higher and C₄₊ are present (Table 3). CH₄ and C₂ can be produced through both, the microbial (biogenic) and thermocatalytic (thermogenic) decomposition of organic matter, whereas C₃₊ alkanes are mainly assigned to thermocatalytic reactions at greater depth (Whiticar, 1999). The ratio of methane to ethane and propane, called the Bernard Factor ($B_f = CH_4/(C_2+C_3)$) is used to distinguish between biogenic and thermogenic pathways for alkane gases (Whiticar, 1999). Batumi Seep displays B_f -values of 2700–3800, indicating a largely biogenic origin, which is in good agreement with data from Pape et al. (2010). At Pechori Mound, however, a B_f of 400 and the presence of C₄₊ and oil strongly supports a thermogenic origin of the gas.

These geochemical inferences are in good agreement with those from visual and seismic observations. At Batumi Seep a wide feeder channel and/or diapiric structure allowing transport of material from greater depth is absent (Wagner-Friedrichs, 2007).

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Instead, an array of near vertical faults is present, some of them penetrating a bottom simulating reflector at ~ 150 mbsf and reaching the seafloor (Wagner-Friedrichs, 2007). This supports major contributions of shallow biogenic gas. At Pechori Mound observations from seismic data indicate that gas-rich sediments and fluids rise through a structure-wide feeder channel that is connected to a diapir below (Wagner-Friedrichs, 2007), which is probably composed of the organic-rich Maikopian Formation, found elsewhere at 1000–4000 m sediment depth (Meredith and Egan, 2002). Assuming a general geothermal gradient of 30°C km^{-1} , the temperature range in the shallower part of these strata is well within the gas production window of 120 – 220°C (Tissot and Welte, 1984). In accordance with these indications, the porewater analysis of Li, B, $\delta^{18}\text{O}$ and $^{87/86}\text{Sr}$ propose a fluid source at higher temperatures ($>100^\circ\text{C}$) from smectite-illite transformation only at Pechori Mound (Reitz et al., 2011).

The difference in gas compositions at the two sites is strongly expressed in the gas hydrate composition (Table 4). Whereas gas hydrates at Batumi Seep contain C_1 and C_2 only, the hydrate samples from Pechori Mound have a C_2/C_3 ratio < 1 , often characteristic for a mixture of gas hydrate structures (Sloan and Koh, 2007). Pure methane hydrates were reported earlier at Batumi Seep (Klaucke et al., 2006; Pape et al., 2010).

5 Conclusions

Combined measurements of gas volumes and high-resolution porewater chlorinity on pressurized cores allow assessing gas hydrate volumes, formation, distribution and origin. At sites in the Eastern Black Sea gas hydrate volumes in shallow sediments are among the highest values known worldwide with up to 24% pv, exceeding average known values by 10% pv. Further investigations will test whether these high gas hydrate volumes represent a local enrichment or are widely distributed in the organic-rich sediments of the anoxic Black Sea. The investigated gas hydrates at the central Batumi Seep occurred mostly at 85–205 cm depth and differences between the chloride-based (140.7 L) and the collected (211 L) CH_4 gas volume indicates currently

active gas hydrate formation not to be resolved from porewater data. Pure methane hydrates at Batumi Seep are fed by the ebullition of biogenic CH₄ gas, whereas at Pechori Mound light hydrocarbons originate from the advection of fluids enriched in thermogenic hydrocarbons and oil.

5 Appendix A

Numerical transport-reaction modelling

A simple 1-D transport-reaction model (Haeckel et al., 2004) was adopted to simulate the observed Cl⁻ data and the corresponding methane hydrate formation. Four chemical species (chloride, methane, sulfate, and gas hydrate) and the porosity change due to hydrate formation were considered.

A1 Model description

A1.1 Porosity

In early diagenetic models the porosity depth distribution, $\phi(x)$, generally does not change significantly with time, and hence, is prescribed by an empirical function fitted to the measured porosity data (Fig. A1). Gas hydrate formation reduces the porosity with time. Thus, porosity was calculated using:

$$\phi(x, t) = \phi_{\infty} + (\phi_0 - \phi_{\infty})e^{-\beta x} - \text{GH}(x, t) \quad (\text{A1})$$

where ϕ_0 = porosity at the sediment surface ($x = 0$), ϕ_{∞} = porosity at infinite depth ($x = \infty$), and GH = porosity reduction due to gas hydrate.

The “true” porosity of hydrate-bearing, near-surface sediments results from a combination of hydrate pieces, gas hydrates filling pore spaces, and hydrate-free sediments. In addition, hydrate pieces displace the original sediment, thus producing fractures.

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Despite an internal porosity close to zero, they do not seal the sediment above the hydrate layer from that below because the pieces are intercalated in the sediment matrix. This complex mechanism needs future investigation before “true” porosity calculations are feasible. For now, we approximate the porosity reduction as if hydrate formation is solely filling the pore space. We are confident that this description leads only to small errors in our results.

A1.2 Advection

Assuming steady state compaction, the burial velocity can be expressed as:

$$w(x, t) = \frac{1 - \phi_{\infty}}{1 - \phi(x, t)} w_{\infty} \quad (\text{A2})$$

where w_{∞} = sedimentation rate at infinite depth.

Since burial and compaction at cold vent sites are much smaller than the upward fluid flow, they can be neglected and the advection rate is:

$$u(x, t) = \frac{\phi_0}{\phi(x, t)} u_0 \quad (\text{A3})$$

where u_0 = fluid flow rate at the sediment surface.

A1.3 Methane hydrate formation

Methane hydrate formation is assumed proportional to the saturation state of methane in the porewater with respect to its equilibrium concentration in the presence of the hydrate phase (L_{GH}):

$$R_{\text{GH}} = k_{\text{GH}} \left(\frac{\text{CH}_4}{L_{\text{GH}}} - 1 \right) \quad (\text{A4})$$

L_{GH} was calculated following (Tishchenko et al., 2005). The kinetic constant k_{GH} has units of volume hydrate by bulk sediment volume and time. Hydrate formation is simulated within the entire modeled sediment column.

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Since hydrate formation withdraws methane from the porewater, the rate of methane consumption (in units of mole CH₄ per volume porewater and time) is related to R_{GH} by:

$$R_M = \frac{\rho_{GH}}{M_{GH}\phi} R_{GH} \quad (A5)$$

5 where ρ_{GH} = density of methane hydrate and M_{GH} = molar weight of natural gas hydrate.

A1.4 Methane gas dissolution

As gas bubbles rise through the sediments they are replenishing the porewater methane content. A first order rate accounts for this dissolution of ascending gas bubbles:

$$R_{MB} = k_{MB}(L_{MB} - CH_4) \quad (A6)$$

10 where methane concentration in equilibrium with the gas phase, L_{MB} , is calculated following (Tishchenko et al., 2005). Methane gas is represented by a source term for methane dissolved in the porewater (Eqs. A6, A15). It is not transported explicitly by the model. L_{GH} and L_{MB} are kept constant during the model runs because the imposed salinity change does not alter the methane equilibrium concentrations significantly enough to affect the model results. Additionally, pressure and temperature are constant in the investigated sediment interval.

15 Finally, based on ROV observations of vigorous ebullition of methane gas bubbles at the seafloor, we believe that the assumption of an inexhaustible methane gas source is justified.

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



A1.5 Anaerobic oxidation of methane (AOM)

As additional reaction affecting dissolved methane concentrations, anaerobic oxidation of methane (AOM) was included:



5 Mathematically, a second-order rate law describes this redox reaction:

$$R_{\text{AOM}} = k_{\text{AOM}} \text{CH}_4 \text{SO}_4^{2-} \quad (\text{A8})$$

where k_{AOM} is the rate constant for AOM.

A1.6 Chloride exclusion

10 During methane hydrate formation chloride is excluded from the hydrate phase and added to the surrounding porewater. This mass change of porewater over time can be expressed as:

$$m_{\text{PW}}^f = m_{\text{PW}}^i - dm_{\text{GH}} \quad (\text{A9})$$

15 where the indices i and f denote the mass of porewater before and after hydrate formation and dm_{GH} is the mass of the precipitated gas hydrate. Converting mass into a volume balance leads to:

$$V_{\text{PW}}^f = V_{\text{PW}}^i - \frac{\rho_{\text{GH}}}{\rho_{\text{PW}}} dV_{\text{GH}} \quad (\text{A10})$$

Thus, the change in chloride concentration, $d\text{Cl}$, can be written:

$$d\text{Cl} = \text{Cl}^f - \text{Cl}^i = \frac{n_{\text{Cl}}^f}{V_{\text{PW}}^f - \frac{\rho_{\text{GH}}}{\rho_{\text{PW}}} dV_{\text{GH}}} - \text{Cl}^i = \frac{n_{\text{Cl}}^i}{V_{\text{PW}}^i - \frac{\rho_{\text{GH}}}{\rho_{\text{PW}}} dV_{\text{GH}}} - \text{Cl}^i \quad (\text{A11})$$

where n_{Cl} = amount of chloride before (i) and after (f) hydrate formation, and $n_{Cl}^f = n_{Cl}^i$, since the total mass of chloride remains constant during hydrate formation. Rearranging gives:

$$dCl = \frac{Cl^i \rho_{GH} dV_{GH}}{\rho_{PW} V_{PW}^i - \rho_{GH} dV_{GH}} = \frac{Cl^i \rho_{GH} dGH}{\rho_{PW} \phi^i - \rho_{GH} dGH} \quad (A12)$$

5 where porosity $\phi = V_{PW}/V_{bulkSed}$ and $dGH = dV_{GH}/V_{bulkSed}$ is porosity change due to methane hydrate formation. The rate of chloride exclusion ($R_{Cl} = dCl/dt$) is related to the hydrate formation rate ($R_{GH} = dGH/dt$) by:

$$R_{Cl} = \frac{dCl}{dt} = \frac{Cl \rho_{GH}}{\rho_{PW} \phi - \rho_{GH} dGH} R_{GH} \approx Cl \frac{\rho_{GH}}{\rho_{PW} \phi} R_{GH} \quad (A13)$$

where the simplification holds when $\rho_{GH} dGH \ll \rho_{PW} \phi$ for small dt .

10 A1.7 Model equations

The model's governing transport-reaction equations are:

$$\text{Chloride: } \frac{\partial \phi Cl}{\partial t} = \frac{\partial}{\partial x} \left(\phi \frac{D_{Cl}}{\theta^2} \frac{\partial Cl}{\partial x} + \phi_0 u_0 Cl \right) + Cl \frac{\rho_{GH}}{\rho_{PW}} k_{GH} \left(\frac{CH_4}{L_{GH}} - 1 \right) \quad (A14)$$

$$\begin{aligned} \text{Methane: } \frac{\partial \phi CH_4}{\partial t} = & \frac{\partial}{\partial x} \left(\phi \frac{D_{CH_4}}{\theta^2} \frac{\partial CH_4}{\partial x} + \phi_0 u_0 CH_4 \right) - \frac{\rho_{GH}}{M_{GH}} k_{GH} \left(\frac{CH_4}{L_{GH}} - 1 \right) \\ & + \phi k_{MB} (L_{MB} - CH_4) - \phi k_{AOM} SO_4^{2-} - CH_4 \end{aligned} \quad (A15)$$

$$\text{Gas hydrate: } \frac{\partial GH}{\partial t} = - \frac{1 - \phi_\infty}{1 - \phi} w_\infty \frac{\partial GH}{\partial x} + k_{GH} \left(\frac{CH_4}{L_{GH}} - 1 \right) \quad (A16)$$

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$$\text{Sulfate: } \frac{\partial \phi \text{SO}_4^{2-}}{\partial t} = \frac{\partial}{\partial x} \left(\phi \frac{D_{\text{SO}_4^{2-}}}{\theta^2} \frac{\partial \text{SO}_4^{2-}}{\partial x} + \phi_0 u_0 \text{SO}_4^{2-} \right) - \phi k_{\text{AOM}} \text{SO}_4^{2-} \text{CH}_4 \quad (\text{A17})$$

where D_i = diffusion coefficients of Cl^- , CH_4 , and SO_4^{2-} corrected for salinity, temperature and pressure (Hayduk and Laudie, 1974; Li and Gregory, 1974), and $\theta^2 = 1 - 2 \ln \phi$ is the tortuosity correction for diffusion (Boudreau, 1997).

This set of partial differential equations was solved numerically within the MATLAB[®] environment. The discretization of Eqs. (A14)–(A17) was done using finite differences and a combination of Dirichlet and Neumann boundary conditions (see Table A1 for details). The initial conditions are based on the steady state profiles of the “no gas hydrate” condition: (i) linearly decreasing Cl^- concentrations with depth, (ii) methane and sulfate profile if only anaerobic oxidation of methane is present and in equilibrium with methane gas phase, (iii) no gas hydrate, and (iv) observed porosity profile.

Five parameters were adjusted by comparing the model result with the observed data: (i) the advection rate (u_0), (ii) the rate constant for hydrate formation (k_{GH}), (iii) the rate constant for gas bubble dissolution (k_{MB}), (iv) the rate constant for anaerobic oxidation of methane (k_{AOM}), and (v) the simulation time (t_{max}).

A2 Model results

A sensitivity analyses was performed to constrain the values of these five fit parameters. The best fit (Fig. A1) to the observed data was achieved for low fluid advection velocities ($u_0 = 0.1 \text{ cm a}^{-1}$) as the measured chloride profile does not show significant curvature, except for the hydrate related anomaly. The rate constant for anaerobic oxidation of methane (k_{AOM}) basically influences the increase in sedimentary hydrate content near the surface because AOM competes with hydrate formation for the available dissolved methane. A minimum AOM rate constant of $k_{\text{AOM}} = 0.03 \text{ mM}^{-1} \text{ a}^{-1}$ is able to resemble a steep increase as it can be inferred from the measured Cl anomaly.

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Diffusion of methane from below is only able to form very little gas hydrate. In order to build up considerable amounts of hydrate (i.e., several % pv) an additional methane source is needed. Therefore methane gas bubble dissolution has been included in the model. This process is also required in order to deliver enough methane to the surface sediments, so that the onset of hydrate formation at a sediment depth of ~85 cm can be resembled (see start of observed Cl anomaly in Fig. A1). The predicted rate constant for methane gas bubble dissolution is $k_{MB} = 0.2 \text{ a}^{-1}$. To balance this increased methane flux to the porewater and keep dissolved methane concentrations at equilibrium with the hydrate phase ($L_{GH} = 87 \text{ mM}$, see Table A1), hydrate formation needs to proceed with a rate constant of at least $k_{GH} = 0.005 \text{ a}^{-1}$. Finally, a simulation time of several hundreds of years (i.e., here 500 a) ensures that the modeled solute concentrations (Cl^- , CH_4 , and SO_4^{2-}) are at steady state; the solid gas hydrate profile is, of course, not at steady state after this time. For a simulation time of 500 a, the model predicts an average hydrate concentration of 15.2% pv. This is in good agreement with the amount calculated from the chloride anomaly (14.4% pv), but 10% pv less than the amount derived from the degassing method (25% pv). However, it is difficult to conclude an age of the Batumi Seep area from this finding, because hydrate related seeps are dynamic systems and methane fluxes can vary over time by orders of magnitude. In contrast, the model simulation assumes a constant methane flux and a constant hydrate formation rate over the entire simulation time.

Appendix B

Degassing characteristics core BS351AP

Methane is the main constituents of the gas collected from pressure core BS351AP with small contributions of ethane and traces of propane and *i*-pentane (Fig. A1). Their ratios vary only slightly (<0.01%). The more significant alterations occur at the beginning and in the end of the degassing. At the start of the degassing this may relate

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to free gas, gas hydrate of slightly different composition or ethane originating from the pore water. Free gas should be released immediately, except volumes are small and caught in the gas hydrate layer where pathways are blocked until gas hydrates start to decompose and overpressure is strong. This process might also explain the spike occurring at about 120 L. At this point opening pathways could have released a minor amount of overpressurised and encased gas leading to the pressure drop in the volume-pressure plot. Pore water degassing should release constituents that are excluded from gas hydrate structure I cages, such as *i*-pentane, which is clearly increasing during the last stage of the degassing, indicating pore water to degas but not during the early degassing. There should be no differences in gas hydrate stability given any of the occurring compositions; therefore only one threshold pressure is present.

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Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Quantifying gas hydrates at Eastern Black Sea vent sitesK. Heeschen et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Table 1. Station information, sulfate depletion depth below core surface and average core porosity.

On Board/Pangea Station Identifier	Location	Latitude	Longitude	Water depth/ m	Core length/ cm	Sulfate depletion depth/ cm	Average porosity
BS351AP/GeoB 9909-2	Batumi	41°57.53 N	41°17.58 E	855	220	25 (50)*	0.721
BS359AP/GeoB 9913-5	Pechori	41°58.99 N	41°07.41 E	1031	106	40	0.680
BS371AP/GeoB 9923-3	Batumi	41°57.62 N	41°17.52 E	859	175	135	0.705
BS378AP/GeoB 9929-2	Batumi	41°57.56 N	41°17.20 E	851	190	50	0.721

* Sediment depth of Core BS351AP was corrected (+25 cm) for porewater data using measurements from video guided multi coring. The core length of 220 cm therefore covers 25–245 cm sediment depth (also see Appendix A).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Table 2. Data from gas collection including volumes of collected gas, CH₄ and gas hydrate as well as dissolved and total CH₄ concentrations in DAPC sediment cores between the depth of sulfate depletion and the core bottom (except BS351AP^{85–205 cm} and BS351AP^{85–205, 88%}).

Station/Core	Core length cm	Collected gas/ L	Air/ %	Collected CH ₄ / L	ΣCH ₄ / mol kg ⁻¹	ΣCH ₄ / mol	CH ₄ (aq)/ mol	GH ¹ / % pv	GH ¹ / % cv
BS351AP ^{50–245 cm}	195	226.2	2.24	221.0	1.206	9.03	0.66	14.6	10.5
BS351AP ^{85–205 cm}	120	226.2	2.24	221.0	1.945	9.03	0.40	24.5	17.7
BS351AP ^{85–205, 88%}	120	226.2	2.24	221.0	1.712	9.03	0.40	21.5	15.5
BS359AP	66	88.7	2.53	86.2	1, 404	3.52	0.22	17.3	12.3
BS371AP	45	10.9	7.16	10.2	0.234	0.41	0.15	1.9	1.6
BS378AP ²	140	200.6	1.96	196.7	1.425	8.04	0.49	17.6	13.3

¹ Assuming a molar CH₄/water ratio of 5.9 in sl gas hydrates, i.e. an occupancy of 90% of the small cages by CH₄ (Ussler and Paull, 2001), resulting in 182 L CH₄ per liter of gas hydrate given STP conditions ($p = 1013 \text{ hPa}$, $T = 298.15 \text{ K}$). (Note: in Heeschen et al., 2007 the CH₄ volume of gas hydrate is based on 273.15 K and 164 L). The CH₄ equilibrium concentration (C_{eq}) is $0.0087 \text{ mol CH}_4 \text{ kg}^{-1}$.

² A clogged valve led to difficulties while opening the liner which causes higher uncertainties regarding the core length and thus the gas hydrate volume (~10%).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Table 3. Average hydrocarbon composition of the collected gas (%) and the Bernard Factor (B_f); n.d. = below detection limit.

Station, Core	C_1 /%	C_2 /%	C_3 /%	i - C_4 /%	n - C_4 /%	i - C_5 /%	B_f
BS351AP	99.966	0.033	0.001	n.d.	n.d.	n.d.	2940
BS359AP	99.634	0.274	0.022	0.055	0.001	0.007	337
BS371AP	99.964	0.024	0.002	n.d.	n.d.	0.007	3845
BS378AP	99.963	0.036	0.001	n.d.	n.d.	n.d.	2701

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Table 4. Gas hydrate compositions from Batumi Seep Cores (BS350G: $n = 4$; BS352G: $n = 1$) and Pechori Mound (BS356G: $n = 1$; BS360G: $n = 3$); n.d. = below detection limit.

Alkane	Batumi Seep		Pechori Mound	
	BS350G	BS352G	BS360G	BS356G
C ₁ /%	99.91	99.71	99.14	97.63
C ₂ /%	0.08	0.28	0.15	0.25
C ₃ /%	n.d.	0.01	0.58	1.64
<i>i</i> -C ₄ /%	n.d.	n.d.	0.10	0.39
<i>n</i> -C ₄ /%	n.d.	n.d.	0.02	0.08

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table A1. Parameters and boundary conditions used in the numerical model.

Parameter	Value
Fixed	
Maximum depth of calculation	500 cm
Temperature	8.0 °C
Pressure	85.5 atm
w_{∞} (sedimentation velocity)	0.02 cm a ⁻¹ ^a
ϕ_0 (porosity at $x = 0$)	0.914(7) ^b
ϕ_{∞} (porosity at $x = \infty$)	0.60(2) ^b
β (porosity attenuation coefficient)	0.008(1) cm ⁻¹ ^b
$[Cl^{-}](x = 0, t)$	360 mM
$[Cl^{-}](x = 500 \text{ cm}, t)$	250 mM
$[CH_4](x = 0, t)$	0 mM
$[CH_4](x = 500 \text{ cm}, t)$	L_{MB}
$[SO_4^{2-}](x = 0, t)$	18 mM
$[SO_4^{2-}](x = 500 \text{ cm}, t)$	0 mM
$GH(x = 0, t)$	0% pv
$dGH/dx _{x=500 \text{ cm}, t}$	0
L_{GH} (CH ₄ equilibrium conc. with GH phase)	87 mM ^c
L_{MB} (CH ₄ equilibrium conc. With gas phase)	113 mM ^c
M_{GH} (molar weight of natural GH)	122.3 g mol ⁻¹ ^d
ρ_{GH} (GH density)	0.9 g cm ⁻³ ^d
ρ_{PW} (mean porewater density, linear Cl ⁻ profile)	1.021 g cm ⁻³ ^e
Adjusted	
t_{max} (simulation time)	500 a
u_0 (porewater advection velocity)	0.1 cm a ⁻¹
k_{GH} (rate constant for hydrate formation)	0.005 a ⁻¹
k_{MB} (rate constant for gas bubble dissolution)	0.2 a ⁻¹
k_{AOM} (rate constant for AOM)	0.03 mM ⁻¹ a ⁻¹

^a Jørgensen et al. (2004).

^b Results of least-squares fit to measured porosity data ($\chi^2 = 0.02$) with 2σ standard deviation given in brackets (last digit).

^c Calculated following Tishchenko et al. (2005).

^d Ussler and Paull (2001).

^e Calculated following Fofonoff and Millard (1983).

BGD

8, 4529–4558, 2011

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



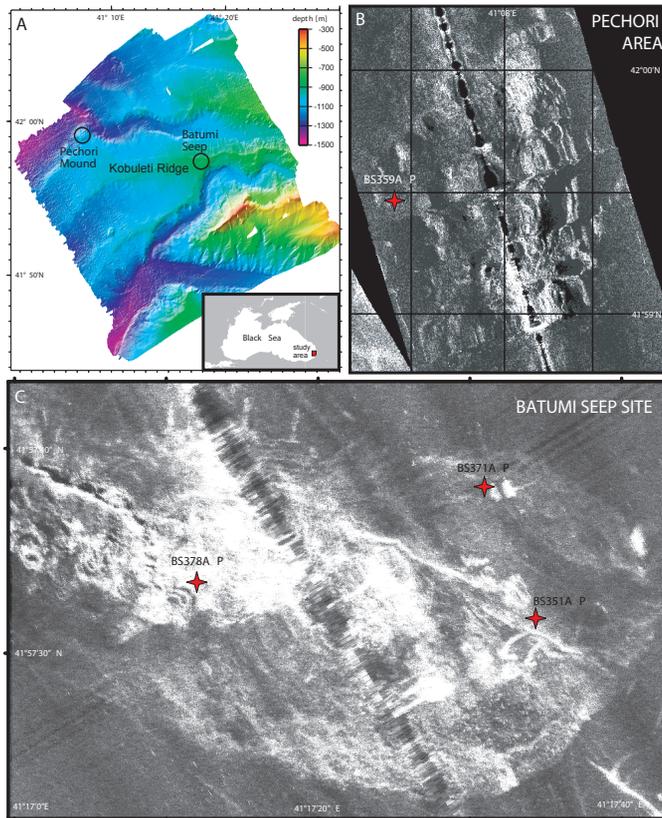


Fig. 1. Working area and coring stations (star symbols and labels) offshore Georgia, eastern Black Sea: **(A)** detailed bathymetric map of the study area. **(B)** 30 kHz MAK Sidescan sonar mosaic of the Pechori area. **(C)** Detailed 75 kHz DTS-1 sidescan sonar mosaic of the Batumi Seep. The high backscatter intensities in **(B)** and **(C)** are shown in light tones and may correlate to the presence of near-surface gas hydrates and authigenic carbonate precipitates (modified after Klaucke et al., 2005).

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



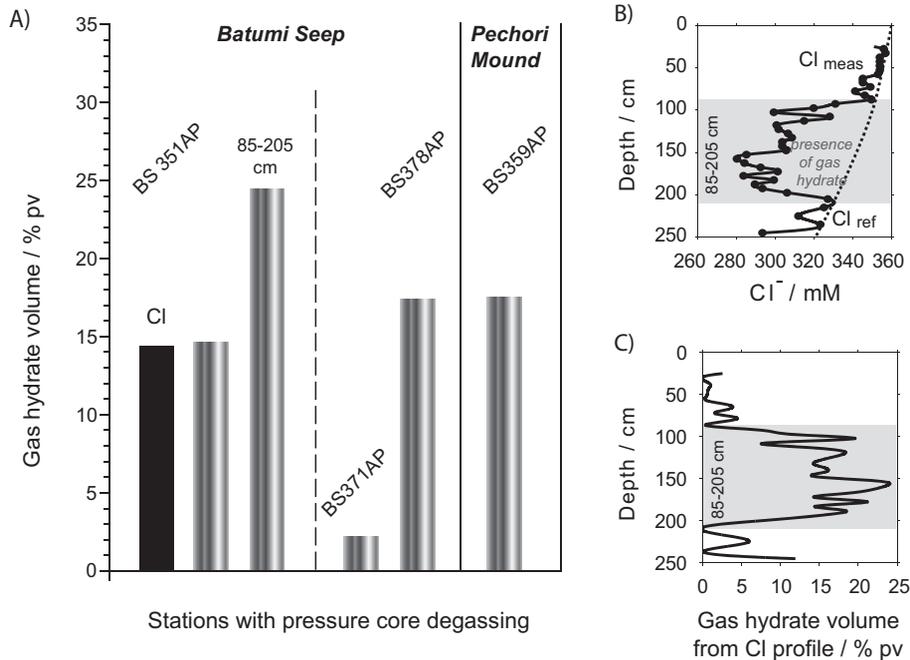


Fig. 2. (A) Gas hydrate volumes in shallow sediments of Batumi Seep and Pechori Mound as calculated from the degassing of the DAPC cores, given in per cent pore volume (% pv). Hydrate volumes for core BS351AP are derived from the degassing (gray columns), the Cl^- profile model in **(B)** and **(C)** (black column, CI), and the volume gained from the combined results of degassing and the chloride measurements, i.e., 211 L CH_4 locked in gas hydrates at core depth between 85 and 205 cm (gray column, 85–205 cm). **(B)** Measured Cl^- concentrations of BS351AP (dots) in comparison to the modeled “in-situ” Cl^- profile (Cl_{ref} , dotted line) characterized by the advection of less saline fluids **(C)** Calculated gas hydrate distribution depth as calculated from Cl^- anomalies and Cl_{ref} in core BS351AP. Sulfate depletion in core with BS351AP is reached at 75 cm core depth. See Sect. 3.3 and Appendix for details on the model.

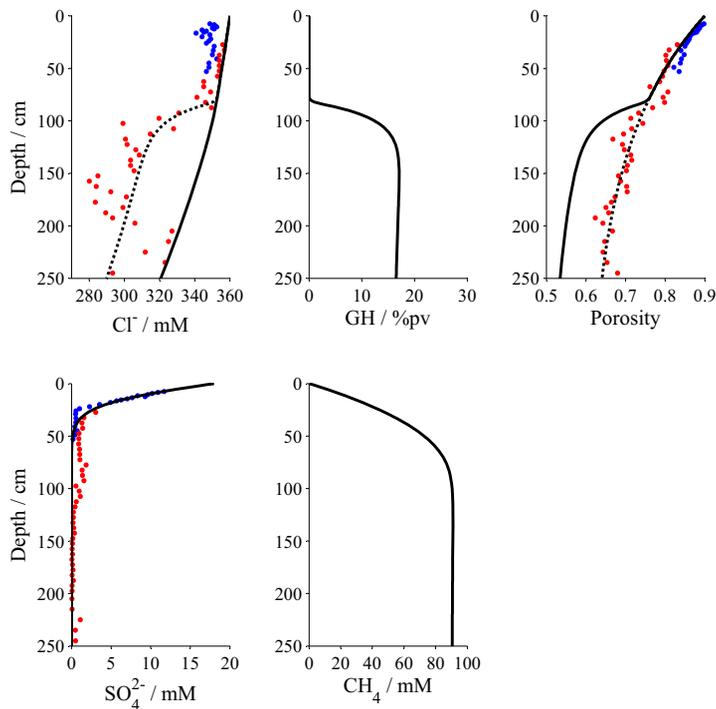


Fig. A1. Result of the numerical 1-D transport-reaction model (solid lines) of gas hydrate formation in the Batumi Seep Area at Site BS 351 DAPC. Plotted data are a combination of BS 351 DAPC (red dots) and BS 369 MC (blue dots). The DAPC core probably lost ~25 cm sediment at the top, as inferred from the measured porosity data, whereas the multicorer liner penetrated too deep and therefore is missing the top 7 cm of the sediment, as inferred from the sulfate data. The values of the adjusted model parameters of this simulation are given in Table A1. The dotted Cl⁻ profile would be observed ex situ after decomposition of all model-predicted methane hydrate. The dotted porosity profile represents the initial depth distribution without hydrate formation as derived from least squares fitting to the data.

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



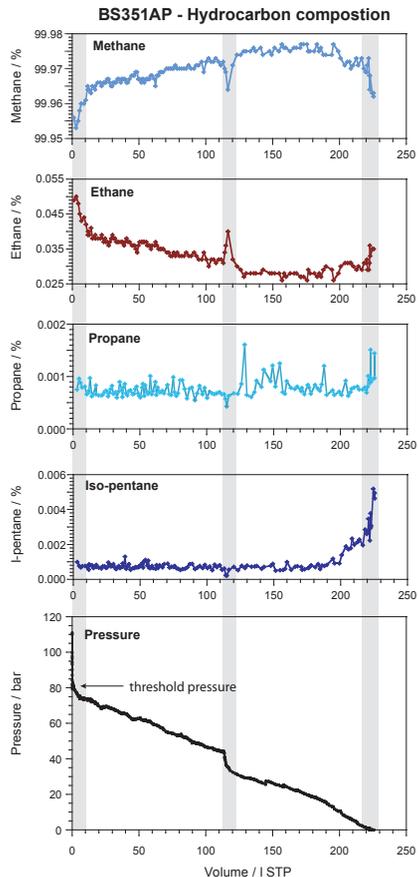


Fig. A2. Changes of gas composition (upper 4 panels) and pressure (lower panel) with increasing gas volume during the degassing of pressure core BS351AP. The gray-shaded boxes indicate areas of enhanced compositional changes, possibly due to free gas occurrences (0–11 L and 112–122 L) and porewater degassing (215–226 L). See text for further discussion.

Quantifying gas hydrates at Eastern Black Sea vent sites

K. Heeschen et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

