

MARINE GAS HYDRATE RESEARCH: CHANGING VIEWS OVER THE PAST 25 YEARS

Erwin Suess
Leibniz-Institute for Marine Sciences (IFM-GEOMAR)
University of Kiel, Germany

ABSTRACT

During the past quarter century views have changed in marine gas-hydrate research and in its perception by the society at large: (1) Deep-sea drilling has gone from a policy of avoiding gas hydrate to emphasizing deliberate drilling for it. (2) International programs have evolved from exploiting gas hydrates as energy to considering exchange of CO₂ for CH₄ hydrates as a means of carbon dioxide storage. (3) Lately, due to global change, research has changed from pursuing methane-hydrate reserves to documenting release of methane from destabilization in marginal seas. The first stage generated a wealth of knowledge and laid the foundation for marine gas hydrate research upon which we build today. The second stage is traced to more accurately estimating exploitable hydrate-bound gas and finding recovery technologies, that has lead to the discovery of an innovative option coupling production of methane from CH₄-hydrate to storage of CO₂ via in the sub-seafloor. Governments worldwide have recognized the potential for carbon dioxide storage and have begun to implement regulations for such environmentally safe carbon capture and storage (CCS). During the third stage, in further exploring global methane hydrate reserves, it has become evident that environmental changes over the past decades may have triggered release of methane from destabilizing hydrate at the seabed as well as diminished oxygen content in the near-bottom of marginal seas. Such scenarios had been proposed for past global warming and now appear to become active again. Exemplary highlights and selected cases studies are documented for each of the evolving stages.

Keywords: gas hydrates, deep-sea drilling; carbon dioxide storage; global change

INTRODUCTION

During the past quarter century fundamental and remarkable changes have occurred in marine gas-hydrate research and in its perception by society at large. Three evolving stages are evident: Deep-sea drilling has gone from a policy of avoiding gas hydrate to emphasizing deliberate drilling for it. Then research has gone from the goal of exploiting gas hydrates as energy to considering exchange of CO₂ for CH₄ hydrates as a means of carbon dioxide storage. Lately, due to global change, research is attempting to document the release of methane from natural hydrate destabilization in marginal seas. Exemplary highlights and selected case studies document each of the evolving stages.

THE FIRST STAGE

From avoiding gas hydrates in deep-sea drilling to dedicated drilling of hydrate

The Deep-Sea Drilling Program and its successors contributed more than any other initiative to bring marine gas hydrate research into focus, generating

an enormous wealth of scientific knowledge, with drilling technology, international research teams and the required pre-site geophysical surveys as ‘drivers’ of this success.

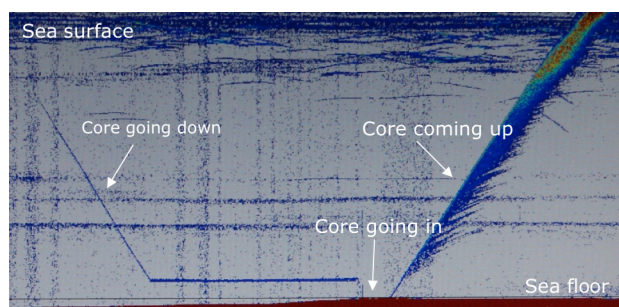
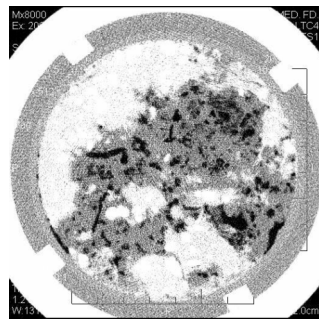


Figure 1: Gas flares indicate degassing of hydrate from sediment core; high-frequency acoustic image of coring operation with ship on station. From A. Obzhirrov, POI, Vladivostok

Gas hydrates were first formally addressed by the Pollution Prevention and Safety Panel of the Ocean Drilling Program (ODP) by recommending

in 1986 that “...drilling should not be carried out into strata underlying the gas hydrate stability zone...” [1]. Later in 1992, based on re-interpretation of seismic data and structural relationships, drilling was recommended by including an interesting qualification: “...beneath visible BSRs in geologic settings that are otherwise considered safe...” [2]. Finally in 2000, during the successor program, the Integrated Ocean Drilling Program (IODP), the COMPLEX initiative enthusiastically endorsed drilling as “...a challenging opportunity for an integrated program of ... to establish an ocean-wide network of hydrate sampling sites...” [3]. Most recently, the INVEST initiative published in 2010 sees the diverse role of marine gas hydrates as a new venture for the coming decade [4]. Among these, geo-hazards, sub-seafloor resources, climate sensitivity, human-Earth interaction and deep biosphere are sub-chapters that spell out future research efforts.

Figure 2 CAT-scan image of hydrate in pressurized core; white = sediment; gray = hydrate; black = free gas. Scale = 10 cm [14]



Not to be neglected, prior to the initial cautious approach by ODP was an “uncharted” period of marine gas hydrate research with DSDP Legs 66, 67 and 84 providing first-hand new knowledge about methane hydrates at convergent margin settings [5]. Among the outstanding results were the recognition of “freshening” of pore waters [6] as an artifact from destabilization and hydrate water release during and immediately after core recovery and that sediment properties responsible for the porosity would favor formation of layers, nodules or disseminated gas hydrates within the stability zone [7].

Gas hydrate drilling during ODP and national program

Over the last 25 years several legs of ODP were either fully or partially dedicated to understanding

marine gas hydrates. Convergent and passive continental margins were targeted [8]. The objectives often addressed fluid flow as well, since only the upper portion of the drill hole was within the hydrate stability field whereas total drilling depth was several 100s of meters below seafloor, well outside the temperature of the gas hydrate stability zone GHSZ [9].

Such large-scale international activities were promptly supplemented by national gas hydrate initiatives [10]. Without exception marine hydrate as potential energy resource was high on the list of priorities of these national programs, summaries of which were presented at the 6th International Congress on Gas Hydrates [11, 12]. Towards the end of the past decade funds spent by national initiatives vastly exceeded those spent on ODP/IODP dedicated gas hydrate research.

A mention of results, examples and case studies here, excluding geophysical advances, include the online compilation of global gas-hydrates distribution [13], the importance of pressure-preservation of drill cores (Figs. 1, 4, 5) [14, 15, 16, 17], infra-red and CAT-scan imaging of hydrate layers in cores (Fig. 2) [18], macro- and micro-fabric studies (synchrotron X-ray cryotomographic microscopy, SRXCTM) [19, 20, 21], the relationship between bottom simulating reflector (BSR; Fig. 3) and the hydrate stability zone including free gas accumulation beneath the BSR [22, 23, 24], the role of fluid flow [9, 25], role of microbes including the discovery of AOM-consortia [26, 27].

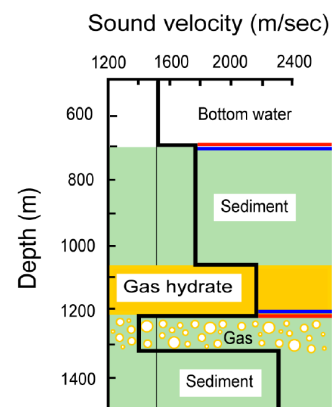


Figure 3 Changes in sound velocity at the sediment/water interface and in the sub-seafloor; interaction of seismic waves with hydrate and free

gas layers generate the bottom-simulating-reflector (BSR); blue-red double line = BSR indicates reverse polarity; red-blue double line at water-sediment interface indicates normal wave polarity [22, 23, 24]

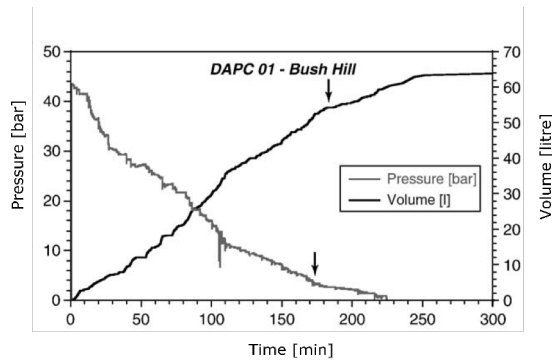


Figure 4 Controlled degassing from pressure core (DAPC) with time; cumulative volume of gas released from hydrate [14,16, 18]

Moreover, the vast number of advances, specializations and the penetration of hydrate-related issues into other fields-- all resulting from dedicated gas-hydrate drilling during ODP and the national programs-- has generated scientific spin-offs as shown below.

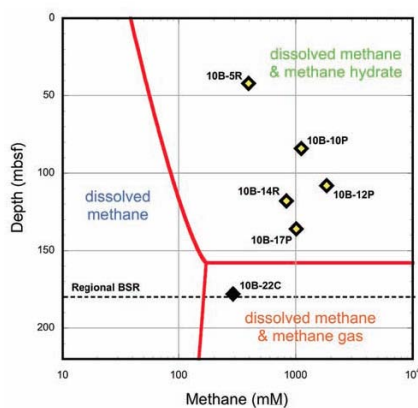


Figure 5 Methane concentrations released from pressurized cores at different water depths in the Ulleung Basin; phase boundaries for solid hydrate-dissolved and free methane confirm presence of hydrate in samples yellow symbols [15,17]

THE SEOND STAGE

From exploiting methane hydrates as energy to storing CO₂ as hydrate

The second stage can be traced to attempting more reliable estimates of exploitable hydrate-bound global gas reserves in marine sediments and to finding recovery technologies. This effort is summed up in the provocative statement [28]: *How much is really out there?* An initial estimate of 10,000 gigatons (Gt = 10¹⁵ g) of hydrate-bound methane carbon [5] stood for a long time until revisions gradually reduced it down to between 2-3 10³ Gt [28].

Table 1

Estimates of global gas reserves from hydrates, regional exploitable deposits and conventional gas reserves; various units from many sources [11, 12, 28, 29, 30, 31, 32, 33, 34]

	CH ₄ carbon Gigatons	Gas (STP) Bill. m ³	Gas (STP) Tcf
Hydrate gas			
<i>in place</i> maximum	>10,000	20,400,000	721,000
low permeability*	1,390	2,830,000	100,000
<i>in place</i> minimum	1,000	2,040,000	72,100
high permeability*	14	28,300	1,000
non-sandstone & others*	139	283,000	10,000
North Slope	1.4	2,830	25-160*
Arctic exploitable*	<1	283	10-100
Japan** eastern Nankai		1,132	40
exploitable	<1	566	20
western Nankai	2.8	5,660	200
Gas reserves 2009			
World, proven	88	176,720	6,250
projected	>500	1,020,000	36,040
USA, proven	3.3	6,735	238
projected	29	58,720	2,075**
Canada, proven***	1.4	28,300	100
projected***	348	707,500	25,000

Gigaton methane-C = 2.04 x 10¹² m³ gas (STP); Billion cubic meters (Intl.) = 10⁹ m³; Tcf = Trillion cubic feet = 28.3 x 10⁹ m³; *2010 estimates; ** Gulf of Mexico, North slope, incl. shale extraction; *** undifferentiated

Furthermore, the petroleum systems approach-- considering reservoir permeability, price, transport and production technology--now places gas-hydrate reserves into the same order of magnitude as conventional natural gas reserves; e.g. a few 10s of Gt [11, 29, 30, 31, 32, 33] with differentiating between maximum and minimum estimates of methane in place and *recoverable methane* [Table 1; 34]. Complicating matters even more, particularly for politicians and the public-at-large whose acceptance in secure energy supplies currently is a prime concern, are the different units being used in expressing methane hydrate reserves. Table 1 lists the most widely used units and their equivalents; e.g. gigatons (Gt) of carbon contained in methane hydrate, billion cubic meters

(Bill. m³) and trillion cubic feet (Tcf) of gas at standard pressure and temperature (STP).

Current recovery scenarios are modifications of technologies used in the oil and gas production. (a) Heating hydrate-containing subsurface strata until temperatures reach the stability limit and free gas forms. Production tests using this approach were successfully conducted in 2002 and 2008 at the on-land permafrost site Mallik in the McKenzie River Delta [32] though scaling and adopting this approach to offshore and sub-seafloor settings is not easily accomplished. (b) Reducing pressure until destabilization occurs is an analogous approach to generate free methane gas. Here efficiency is higher because less energy is consumed than in heating. Advanced planning has been underway in Japan to implement the pressure-reduction technology by 2014 at the exploitable sites of the eastern Nankai Trough. (c) Injection of chemical additives to reduce stability is another approach but appears less favored because of problems in avoiding damage to the environment.

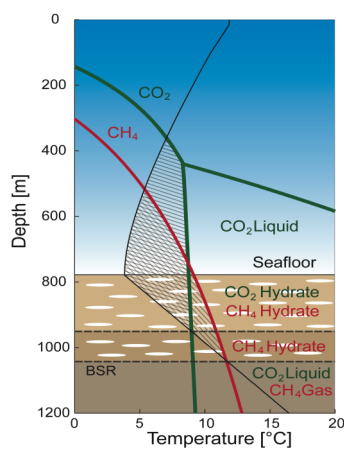
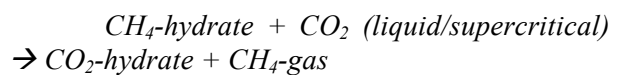


Figure 6 Stability of CH₄-hydrate (red) and CO₂-hydrate (green); within the overlapping shaded area both phases exist; at pressures equivalent to 800-1000 m water depth spontaneous exchange of CO₂ for CH₄ takes place [34, 35, 36]

A promising new technology for recovery of natural gas from hydrates injects supercritical liquid CO₂ from fossil-fuel power plants into methane hydrate strata. Hereby, liquid CO₂ spontaneously transforms methane hydrate into carbon-dioxide hydrate, liberating methane [36].



Heat is liberated during this transformation because CO₂-hydrate is more stable than CH₄-hydrate. Therefore, CO₂-addition stimulates methane liberation and generates heat for continued hydrate destabilization (Fig. 6). In several laboratory tests around the world this transformation has been accomplished but its rate is slow and ceases at some point [35, 36]. Research is underway to increase the reaction rate through varying pressure reduction, temperature increase, and CO₂-supply.

Storage of CO₂ as hydrate in continental slope sediments appears more safe, albeit more expensive, than current offshore options in geologic formations beneath the shelves. CO₂-storage options are shown in Figure 7 [34]. Currently storage in depleted oil and gas reservoirs, mostly on land, is widely favored as it enhances residual hydrocarbon recovery although total storage capacity and degree of safety remain unclear.

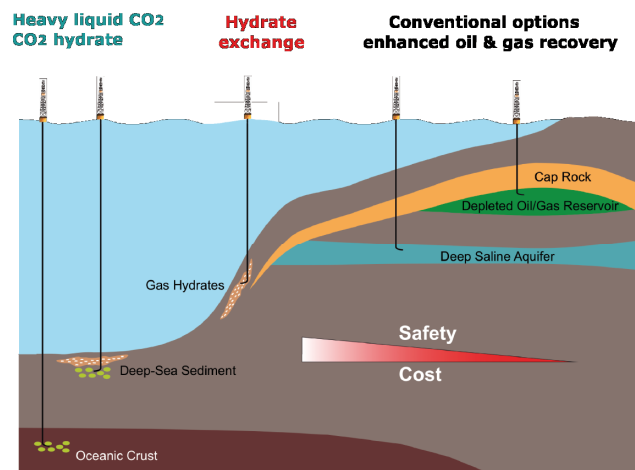


Figure 7 Current options for offshore CO₂-storage; shallow depth injection into depleted oil and gas reservoirs enhances hydrocarbon recovery; at greater depths both CO₂-/CH₄-hydrate exchange and storage as heavy liquid are envisioned [37, 38]

Storage in saline aquifers is a proven option for both shallow offshore and on-land formations [38] whereas CO₂-storage as hydrate or as heavy liquid has not been demonstrated on an industrial scale

[35, 36, 37]. The option of storing CO₂ as a heavy liquid results from the different compressibility between seawater and liquid CO₂. At pressures exceeding the equivalent water depths of >3000 m the density of liquid CO₂ is higher than that of seawater so it may remain trapped at a specific depth window below the seafloor [37].

Governments worldwide recognize the potential for carbon-dioxide storage and have begun to implement technical, economic and administrative regulations for environmentally safe Carbon Capture and Storage (CCS). Updated information on international and national developments is readily available from the Carbon Capture Journal [38]. Regulations so far favor using land-based geological formations and those extending sub-sea in relatively shallow waters; however, CO₂-hydrate formation, CO₂-CH₄-hydrate exchange and storage of gravitationally stable CO₂-liquid in sub-seabed formations require pressures and temperatures that exist at water depths down to 3000 m. Generally, it seems prudent to advance research and testing for environmentally friendly disposal of carbon dioxide including storage coupled with methane recovery while considering the environmental impact of both activities.

THE THIRD STAGE

From pursuing global hydrate deposits to documenting methane release due to global change

Further exploring of global methane hydrate reserves surprisingly yielded evidence that environmental changes over the past decades may have triggered natural release of methane from decomposing hydrate at the seabed as well as slowed consumption of methane in the water column. Regions where such recent changes might be identified are the Arctic shelves and margins and the Black Sea. At the Svalbard margin recent bottom-water warming may be responsible for the release of large quantities of methane from the seabed.

A 30 year record shows an increase of 1 °C [39]. At the site near-surface gas hydrates appear to be in contact with warmer bottom waters. Warming shrinks the vertical extent of the gas hydrate stability zone (GHSZ) causing methane to escape from decomposing hydrate (Fig. 8).

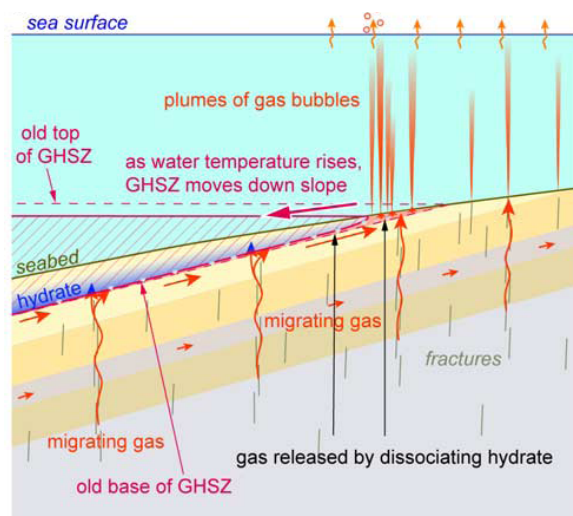


Figure 8 Escape of methane from sediments of the Svalbard margin; scenario due to recent increase in bottom water temperature; hereby gas hydrate stability zone (GHSZ) contracts at the BSR-outcrop and releases free gas from below [39]

This is supposedly evident in methane plumes emanating from the site where hydrates appear to be in closest contact with bottom water. Long-term records of methane plumes at that particular site are, however, not available. Currently the debate centers on the rate of heat conduction through the seabed to sub-seafloor hydrates. Tentatively, hydrate layers found <3 m below the seafloor could be affected by warming of bottom water over about 30 years.

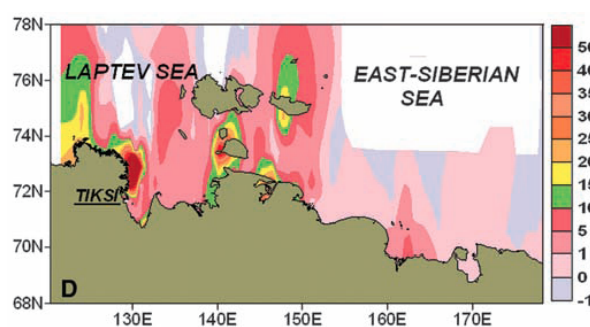


Figure 9 Flux of methane to the atmosphere from surface wates of the Laptev Sea; units = mg m² d⁻¹ thawing permafrost and gas hydrate destabilization contribute to gas emission [40]

The wide Laptev Sea shelf is underlain by permafrost and hydrates and is a region of vast

methane emissions to the atmosphere. Recently the summer methane flux to the atmosphere was quantified [40]. The authors leave open whether methane release results from recent global or seasonal warming or from increased warmer inflow of the Lena River but favor release from hydrates (Fig. 9).

The shelf of the Barents Sea is another region vulnerable to hydrate destabilization from change in bottom water temperature. Currently bottom waters of near-zero temperature flow from the Arctic Ocean over the Barents Sea shelf, keeping methane hydrates stable in the underlying sediments [41]. The predicted warming of bottom waters over the next century however will expose these sub-seafloor hydrates to temperatures well outside the (GHSZ) [42] and hence may generate a vast methane flux to the atmosphere (Fig. 10).

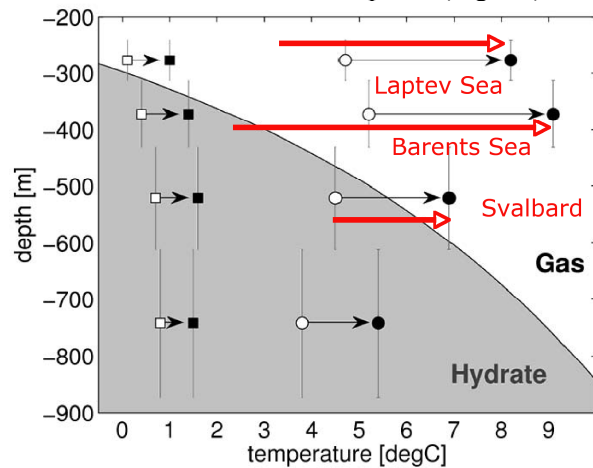


Figure 10 Temperature changes from global warming in the Arctic Ocean and the European Northern Seas (open squares = Arctic Ocean; open circles = shelf and margin sites; closed symbols = predict.); superimposed methane hydrate stability field [42]; Laptev Sea = currently degassing [40]; Svalbard margin = vulnerable to degassing [39]; Barents Sea = currently degassing; vulnerable to future and past catastrophic degassing [41, 43, 44].

Interestingly, such changes in temperatures might have also occurred in the past. There is evidence for hydrate destabilization at the shelf from explosive craters at the sea floor [43]. These are no ordinary pockmarks, but they appear to show a relationship to the underlying gas hydrates [44].

Admittedly, all case studies from the Arctic Ocean are currently inconclusive as to the central question of whether or not change already is active from the positive feedback of accelerated global warming. However, such scenarios have been proposed for well-documented warm periods in the Earth's history [45, 46]. Closely related to hydrate destabilization from global warming are slope failures. Again the Earth's history provides numerous examples; the most prominent of which is the Storegga slide off the Norwegian coast [47]. Emplacement of the slide mass into the central Norwegian Sea occurred in several events [48]. Each large enough to have caused tsunamis that affected the surrounding coasts off Iceland and Scotland as well as the Faeroe and Shetland islands. This gas hydrate related scenario inspired a science fiction novel [49] with vastly exaggerated global impact.

Another scenario related to global change invokes accelerated methane released into the atmosphere from hydrate destabilization in Black Sea sediments. Increased methane input as previously discussed for warming of sediments on the Arctic shelves may in the Black Sea be seriously aggravated by slowed consumption of methane due to an expanded oxygen-deficient upper water column. Currently methane input to the Black Sea basin from seeps and gas hydrates appears to be almost balanced by oxidation in the upper water column such that little methane escapes to the atmosphere [50]. However, several lines evidence point to a scenario of how this situation might change as a consequence of global change. Over the broad northwestern shelf areas off the Ukraine, Romania and Bulgaria, 1000s of methane seeps have been mapped [51]. Other areas are just being investigated but quite possibly are equally strong emitters of methane to the water column [50, 52]. Overwhelmingly, the methane plumes are concentrated at water depths close to and above the equivalent pressure of the methane-hydrate stability field. This and the sub-seafloor dissolved gas front suggest that hydrate stability currently suggesting increased methane input. regulates methane emissions [50, 51] Bottom water warming would readily cause seepage to increase over the present seep activity.

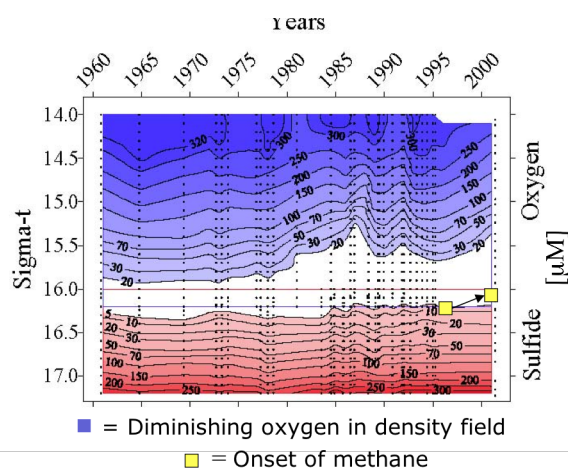


Figure 11 Evidence for shoaling of the oxic/anoxic interface in the water column of the Black Sea over the last 40 years [54]; oxygen and sulfide concentrations [μM]; Sigma-t = density ρ (rho) – 1000 in kg m^{-3} is used to eliminate concentration changes caused by circulation and mixing of different water masses; time-series methane data are sparse; onset of methane over the last decade coincides with observed shoaling [55, 56]

The body of the Black Sea water contains an enormous pool of dissolved methane mostly below the oxic/anoxic interface [50, 53]. Methane reaching the oxygenated water above the interface, by exchange or by directly seeping from shallow shelf depth, is consumed by microbes utilizing oxygen (methyloctrophy). Methane remaining below the interface or seeping from the seafloor directly into the anoxic waters is also consumed by microbes utilizing sulfate (AOM). These mechanisms currently regulate the methane budget with most of it originating from hydrates and seeps and little escaping into the atmosphere [50, 52].

There has been a long-standing debate whether or not the oxygenated shallow-water layer in the Black Sea diminishes in thickness due to global/anthropogenic change [54, 55]. Evidence for such a long-term change on a basin-wide scale is difficult to obtain. Dissolved oxygen and sulfide data show that indeed over the past 40 years the density surface separating anoxic from oxic waters may have become shallower (Fig. 11). Coincident with shoaling is the first appearance of methane between 1990-2000 [56, 54]. If this trend continues and anoxic waters spread over the

shelves such that more seeps emit methane into that layer, then the methane balance might be disturbed. If additional warming succeeds in increasing seepage from hydrate destabilization then the methane consumption potential may be overwhelmed causing an increased flux to the atmosphere. Again, the evidence for increased methane flux from the bottom of the Black Sea is not entirely clear nor the effect on the methane balance if the oxic water layer shoals, yet the scenario (EUXPOND) is perfectly convincing as to the central question of whether or not global change is already active from accelerating global warming as postulated by many [57, 58].

PERSISTENT QUESTIONS

In spite of the advances and the stage of maturity reached in marine gas-hydrate research, new and old questions persist. Deriving estimates of **accurate global and exploitable hydrate reserves** remains high on the priority list and efforts are continuing. Closely connected is the question of **hydrate saturation**, i.e., the degree of sediment pore space occupied by gas hydrates. Pressure coring and controlled release of methane, “freshening” of pore waters as well as geophysical modeling are currently in use. Up- or down-scaling of these results to stratigraphic units containing hydrates is not readily possible. **Macro- and micro-imaging** techniques have just begun to yield results on grain boundaries and sizes, phase changes and inclusions all of which affect physical properties of gas hydrates. Application is seen for advances in basic knowledge but also for seismic-wave propagation and related geophysical modeling. Among new and improved **detection methods** for marine gas hydrates are the controlled source electromagnetic (CSEM) surveys utilizing high electrical resistivity of solid hydrates as compared to host lithologies. As it has become abundantly clear that the majority of methane seeps are fed by sub-seafloor gas hydrates, a global estimate of the “**geogenic**” **flux** has still not been put forward. **Impact on the environment** was discussed above for Stage three and will continue to be a major scientific objective. This includes the impact of global change on natural marine- and permafrost-hosted gas hydrates as well as the potential impact of industrial hydrate production for energy. Effects

will not necessarily be restricted to the anticipated climate feedback but must include continental slope stability factors, as well as stability of the infrastructure needed for energy production. Issues related to environmental impact from industrial gas production depend on the **technologies to exploit hydrates**. For this author the coupled exchange of CH₄-hydrate for CO₂-hydrate in offshore geologic settings as discussed under Stage Two is by far the best option considering the large capacity for CO₂-storage and the safety inherent in dealing with solid CO₂ instead of gaseous or liquid phases as in other storage options.

REFERENCES

- [1] Emeis KC, Kvenvolden KA. *Shipboard Organic Geochemistry on JOIDES Resolution*, Ocean Drilling Program, Tech. Note 7, 1986; p. 23.
- [2] JOIDES Pollution Prevention and Safety Panel Ocean Drilling Program, *Guidelines for Pollution Prevention and Safety*. JOIDES Journal 1992; 18(7) p. 17.
- [3] Pias NG, Delaney ML, editors. *COMPLEX: Conference on Multiple Platform Exploration of the Ocean*. Ocean Drilling Program, 2000; 226 pp.
- [4] Ravelo C, Bach W, Behrmann J, Camoin G, Duncan R, Edwards K, Gulick S, Inagaki F, Palike H, Tada R, editors. *INVEST Report: Defining The New Goals of an International Drilling Program*; 2010. 160 pp., [http://iodp.org/weblinks/ Featured-Publications-HOME-PAGE/INVEST](http://iodp.org/weblinks/Featured-Publications-HOME-PAGE/INVEST)
- [5] Kvenvolden KA. *Gas hydrates – geological perspective and global change*. Rev. Geophys. 1993; 31:173-187.
- [6] Hesse R, Harrison WE. *Gas hydrates (clathrates) causing pore water freshening an oxygen isotope fractionation in deep-water sedimentary environments*. Earth Planet. Sci. Letts. 1991; 55:453-462.
- [7] Ginsburg G, Soloviev V, Matveeva T, Andreeva I. *SEDIMENT GRAIN-SIZE CONTROL ON GAS HYDRATE PRESENCE, SITES 994, 995, AND 997*. In: Paull CK, Matsumoto R, Wallace PJ, Dillon WP, editors. *Proceedings of the Ocean Drilling Program Scientific Results 2000*; 164:237-245.
- [8] Becker K, editor. *Achievements and Opportunities of Scientific Ocean Drilling: The Legacy of the Ocean Drilling Program*. JOIDES Journal 2002; 28(1) 100 pp.
- [9] Fischer AF. *The dynamics and significance of fluids within the seafloor*. In: Becker K, editor. *Achievements and Opportunities of Scientific Ocean Drilling*. JOIDES Journal 2002; 28(1):39-44.
- [10] Suess E, Thiede J, editors. *Gashydrate im Geosystem*. Forschungszentrum Jülich GmbH, Projektträger BEO, Rostock-Warnemünde 1991; 64 pp.
- [11] International Conference on Gas Hydrates, Vancouver BC, Canada; University of British Columbia; *National gas hydrate initiatives by search codes as follows: 1022 for India; 1177 for China; 2232-2235 for Mallik; 1167 for Alaska; 1095 for Japan; 1162 for Korea; 2291-2292 for Taiwan*; <https://circle.ubc.ca/handle/2429/1022>
- [12] Boswell R. *Is gas hydrate energy within reach?* Science 2009; 325:957-958.
- [13] Kvenvolden KA, Lorenson TD. *A global inventory of natural gas hydrate occurrence*. United States Geological Survey; continually updated map and locations to be found under <http://walrus.wr.usgs.gov/globalhydrate/>
- [14] Abegg F, Hohnberg HJ, Pape T, Bohrmann G, Freitag J. *Development and application of pressure-core-sampling systems for the investigation of gas- and gas-hydrate-bearing sediments*. Deep-Sea Res.-I 2008; 55(11):1590-1599.
- [15] Schultheiss PJ, Aumann TJ, Humphrey GD. *Pressure coring and pressure core analysis for the upcoming Gulf of Mexico Joint Industry Project Coring Expedition*. Offshore Technology Conference 2010; Houston, Texas, Contr. 20827
- [16] Heeschen KU, Hohnberg HJ, Haeckel M, Abegg F, Drews M, Bohrmann G. *Hydrocarbon concentrations from pressurized cores in surface sediments, Northern Gulf of Mexico*. Marine Chemistry 2007; 107:498-515.
- [17] Park KP, Bahk JJ, Holland M, Yun TS, Schultheiss PJ, Santamarina C. *Improved pressure core analysis provided detailed look at Korean cores*. In: Methane Hydrate Newsletter, Winter 2009; National Energy Technology Laboratory, US Department of Energy, p. 18-20.
- [18] Abegg F, Bohrmann G, Freitag J. *Marine gas hydrate: Fabric, quantification and free gas content. Examples from Hydrate Ridge-Cascadia*

- margin. Acoustical Society of America Journal 2003; 114(4):2317-2317.
- [19] Klapp SA, Klain H, Kuhs W. *First determination of gas hydrate crystallite size distributions using high-energy synchrotron radiation*. Geophys. Res. Letts. 2007; 34:L13608, doi:10.1029/2006GL029134
- [20] Murshed MM, Klapp SA, Enzmann F, Szeder T, Huthwelker T, Stampanoni M, Marone F, Hintermüller Ch, Bohrmann G, Kuhs WF, Kersten, M. *Natural gas hydrate investigations by synchrotron radiation X-ray cryo-tomographic microscopy (SRXCTM)*. Geophys. Res. Letts. 2008; 35, L23612, doi:10.1029/2008GL035460
- [21] Suess E, Bohrmann G, Rickert, D, Kuhs W, Torres M, Trehu A, Linke P. (2002). *Properties and near-surface methane hydrates at Hydrate Ridge, Cascadia Margin*. Proc. 4th International Conference on Gas Hydrate 2002, Yokohama, 740-744.
- [22] Holbrook WS, Hoskins H, Wood WT, Stephen RA, Lizarralde D, Leg 164 Science Party. *Methane hydrate, bottom-simulating reflectors, and gas bubbles: Results of vertical seismic profiles on the Blake Ridge*. Science 1996; 273:1840-1843.
- [23] Tinivella U, Lodolo E. *THE BLAKE RIDGE BOTTOM-SIMULATING REFLECTOR TRANSECT: TOMOGRAPHIC VELOCITY FIELD AND THEORETICAL MODEL TO ESTIMATE METHANE HYDRATE QUANTITIES*. In: Paull CK, Matsumoto R, Wallace, PJ, Dillon WP, editors. Proceedings of the Ocean Drilling Program, Scientific Results, 2000; 164:273-281.
- [24] Haacke RR, Westbrook GK, Hyndman RD. *FORMATION OF THE BOTTOM-SIMULATING REFLECTOR AND ITS LINK TO VERTICAL FLUID FLOW*. Proceedings of the 6th International Conference on Gas Hydrates, 2008; Vancouver, B.C, Canada
- [25] Suess E. *Marine cold seeps*. In: Timmis KN, editor. *Handbook of Hydrocarbon and Lipid Microbiology*. 2010; 1(3):187-203; Springer Heidelberg, doi 10.1007/978-3-540-77587-4_12.
- [26] Boetius A, Ravensschlag K, Schubert CJ, Rickert D, Widdel F, Gieseke A, Amann R, Jørgensen BB, Witte U, Pfannkuche O. *A marine consortium apparently mediating anaerobic oxidation of methane*. Nature 2000; 407:623–626.
- [27] Jørgensen BB, Boetius A. *Feast and famine - microbial life in the deep-sea bed*. Nature Rev. Microbiol. 2007; 5:770-781
- [28] Milkov AV. *Global estimates of hydrate-bound gas in marine sediments: how much is really out there?* Earth-Science Reviews 2004; 66(3-4):183–197.
- [29] Boswell R, Hunter R, Collett T, Digert S, Hancock S, Weeks M. *INVESTIGATION OF GAS HYDRATE-BEARING SANDSTONE RESERVOIRS AT THE "MOUNT ELBERT" STRATIGRAPHIC TEST WELL, MILNE POINT, ALASKA*. Proceedings of the 6th International Conference on Gas Hydrates 2008, Vancouver, British Columbia, Canada
- [30] Buffett B, Archer D. *Global inventory of methane clathrate: sensitivity to changes in the deep ocean*. Earth and Planet. Sci, Letts. 2004; 227:185-199.
- [31] Dallimore SR. *Overview of energy-related studies of gas hydrates in Canada*. Exploration Industry Workshop, 2009, Calgary
- [32] Dallimore SR, Collett TS, editors. *Scientific Results from Mallik 2002 Gas Hydrate Production Research Well Program, Mackenzie Delta, Northwest Territories, Canada*. Geol. Survey of Canada 2005; Bulletin 585
- [33] *International Energy Outlook 2009*. Energy Information Administration, United States Department of Energy (DOE); www.eia.doe.gov
- [34] Suess E, Haeckel M. *Gashydrate im Meeresboden*. Geographische Rundschau 2010; 5:22-28, Westermann, Braunschweig
- [35] Graue A, Kvamme B, Zornes DR, Stevens JC, Howard JJ, Baldwin BA. *Production of free gas by gas hydrate conversion*. 2007 US Patent 7,222,673 B2
- [36] Graue A, Kvamme B, Baldwin BA, Stevens JC, Howard JJ, Aspenes E, Ersland G, Husebø J, Zornes D. *Environmentally friendly CO2 storage in hydrate reservoirs benefits from associated spontaneous methane production*. Offshore Technology Conference 2006; Houston, Texas.
- [37] House KZ, Schrag DS, Harvey ChF, Lackner KS. *Permanent carbon dioxide storage in deep-sea sediments*. Proc. National Academy of Sciences 2006; 103(33):12291-12295
- [38] Carbon Capture Journal. *Information source for new technical developments, opinion, regulatory and research activity with carbon capture, transport and storage*. 2nd Floor, 8 Baltic Street East, London EC1Y 0UP; www.carboncapturejournal.com
- [39] Westbrook GK, Thatcher KE, Rohling EJ, Piotrowski AM, Pälke H, Osborne AH, Nisbet

- EG, Minshull TA, Lanoiselle M, James HR, Hühnerbach V, Green D, Fisher RE, Crocker AJ, Chabert A, Bolton C, Beszczynska-Möller A, Berndt C, Aquilina A. *Escape of methane gas from the seabed along the West Spitzbergen continental margin*. Geophys. Res. Letts. 2009; 36: L15608, doi:10.1029/2009GL03919
- [40] Shakova NI, Semiletov A, Salyuk V, Yusupov, Kosmach D, Gustafsson O. *Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic shelf*. Science 2010; 327, 1246-1250
- [41] Lammers, S, Suess E, Hovland M. *A large methane plume east of Bear Island (Barents Sea); Implications for the methane cycle*. Geol. Rundschau 1995; 84:59-66.
- [42] Biastoch A, Treude T, Rüpke LH, Riebesell U, Roth C, Burwicz EB, Park W, Latif M, Böning CW, Madec G, Wallmann K. *Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification*. Geophys. Res. Letts. 2011; in press
- [43] Long, D, Lammers S, Linke P. *Possible hydrate mounds within large sea-floor craters in the Barents Sea*. Geological Society, London, Special Publications 1998; 137:223-237.
- [44] Solheim A, Elverhoi A. *Gas related seafloor craters in the Barents Sea*. Geo-Mar. Letts. 1993; 13:235-243.
- [45] Dickens GR, O'Neil JR, Rea DK, Owen RM. *Dissociation of oceanic methane hydrates as a cause of the carbon isotope excursion at the end of the Paleocene*. Paleoceanography 1995; 10:965–971.
- [46] Kroon D, Norris RD, Wilson P. *Exceptional global warmth and climatic transients recorded in ocean sediments*. In: Becker K, editor. *Achievements and Opportunities of Scientific Ocean Drilling: The Legacy of the Ocean Drilling Program*. JOIDES Journal 2002; 28(1):11-15.
- [47] Bünz, S, Mienert J, Berndt C, *Geological controls on the Storegga gas-hydrate system of the mid-Norwegian continental margin*. Earth and Planetary Science Letters 2003; 209: 291–307.
- [48] Micallef A, Masson DG, Berndt Ch, Stow DAV. *Development and mass movement processes of the north-eastern Storregga Slide*. Quaternary Science Review 2009; 28:433-448.
- [49] Schätzing, F. *The Swarm - A Novel*. New York 2006, Regan Books, 881 pp.
- [50] Kessler JD, Reeburgh WS, Southon J, Seigert R, Michaelis, W, Tyler, SC, *Basin-wide estimates of the input of methane from seeps and clathrates to the Black Sea*. Earth & Planet. Sci. Letts. 2006; 243:366-375
- [51] Naudts L, Greinert J, Artemov Y, Staelens P, Poort J, Van Rensbergen P, De Batist M. *Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea*. Mar Geol. 2006; 227:177-199.
- [52] Vassilev A, Dimitrov L. *Spatial and quantity evolution of the Black Sea gas hydrates*. Russian Geology & Geophysics 2002; 43:(7) 672-684.
- [53] Schmale O, Haeckel M, McGinnis DF. *Response of the Black Sea methane budget to massive short-term submarine inputs of methane*. Biogeosciences Discuss. 2010; 7:9117–9136, doi:10.5194/bgd-7-9117-2010
- [54] Konovalov SK, Murray J W. *Variations in the chemistry of the Black Sea on a time scale of decades 1960–1995*. Journal of Marine Systems 2001; 31:217–243.
- [55] Yakushev EV, Chasovnikov EV, Debolskaya EI, Egorov AV, Makkaveev PN, Pakhomova SV, Podymov OI, Yakubenko VG. (2006) *The northeastern Black Sea redox zone: Hydrochemical structure and its temporal variability*. Deep-Sea Research II 53, 1769–1786.
- [56] Egorov AV. *On distribution of methane in the Black Sea water column*. In: Zatsepin AG, Flint M V, editors. *Complex Investigation of the Northeastern Black Sea*. Nauka, Moscow, 2002; 144–147 (in Russian).
- [57] Archer D. *Methane hydrate stability and anthropogenic climate change*. Biogeoscience 2007; 4:521–544.
- [58] Kvenvolden KA. *Potential effects of gas hydrate on human welfare*. Proc. Natl. Acad. Sci. 1999; 96:3420-3426.

