Global estimates of hydrate-bound gas in marine sediments: how much is really out there?

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Abstract

It is generally assumed that oceanic gas hydrates contain a huge volume of natural gases, mainly methane. The most widely cited estimate of global hydrate-bound gas is 21×10^{15} m^3 of methane at STP (or $\sim 10,000$ Gt of methane carbon), which is proposed as a "consensus value" from several independent estimations. This large gas hydrate reservoir is further suggested as an important component of the global carbon cycle and as a future energy source. Here, I present a revised and updated set of well-justified global estimates and discuss how and why they changed over time. It appears that the global estimates of hydrate-bound gas decreased by at least one order of magnitude from 1970s–early 1980s (estimates on the order of 10^{17}–10^{18} m^3) to late 1980s–early 1990s (10^{16} m^3) to late 1990s–present (10^{14}–10^{15} m^3). The decrease of estimates is a result of growing knowledge of the distribution and concentration of gas hydrates in marine sediments and ongoing efforts to better constrain the volume of hydrate-bearing sediments and their gas yield. These parameters appear to be relatively well constrained at present through DSDP/ODP drilling and direct measurements of gas concentrations in sediments. The global estimate of hydrate-bound gas that best reflects the current knowledge of submarine gas hydrate is in the range $(1-5) \times 10^{15}$ m^3 (~ 500–2500 Gt of methane carbon). A significantly smaller global gas hydrate inventory implies that the role of gas hydrates in the global carbon cycle may not be as significant as speculated previously. Gas hydrate may be considered a future energy source not because the global volume of hydrate-bound gas is large, but because some individual gas hydrate accumulations may contain significant and concentrated resources that may be profitably recovered in the future.
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1. Introduction

Natural gas hydrate—a crystalline mineral composed of water and gases (mainly methane)—has been subjected to numerous laboratory and field studies in the past decade including three dedicated Ocean Drilling Program (ODP) Legs: 146 (Westbrook et al., 1994), 164 (Paull et al., 1996) and 204 (Tréhu et al., 2003). The main driving force in gas hydrate research is the common assumption that the global gas hydrate inventory contains a huge amount of methane carbon (Kvenvolden, 1999) and therefore may be both a potential energy resource (Collett, 2002) and a significant player in the global carbon cycle (Dickens, 2001b; Kvenvolden, 2002). However, the global estimates of hydrate-bound gas in marine

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sediments vary by several orders of magnitude and are thought to be highly uncertain (Kvenvolden, 1999; Lerche, 2000).

Makogon (1966) was apparently the first to publish a methodology of estimating hydrate-bound gas in the subsurface, although the first gas hydrate samples were recovered much later (Yefremova and Zizchenko, 1974). Around 20 global estimates of submarine gas hydrate have been published over the last 30 years, the earliest by Trofimuk et al. (1973) and the latest by Milkov et al. (2003). Kvenvolden (1999) analyzed a subset of the global estimates (Table 1) and suggested that 21×10^{15} m³ of methane (or ~ 10,000 Gt of methane carbon, Kvenvolden and Lorenson, 2001) should be considered as a "consensus value" because some independent estimates (e.g., by Kvenvolden, 1988; MacDonald, 1990) converge around that value. The value 10,000 Gt of methane carbon is currently used to justify gas hydrate research (e.g., Wood et al., 2002; Hesse, 2003) and is incorporated into the models of the global organic carbon cycle (Kvenvolden, 2002). However, Lerche (2000) attempted a statistical analysis of some estimates listed by Kvenvolden (1999) and found no systematic pattern of convergence of the published estimates. Moreover, a careful examination of the literature suggests that some estimates listed by Kvenvolden (1999) were never presented (e.g., Makogon, 1981; Dickens et al., 1997), others were cited erroneously (e.g., Trofimuk et al., 1977; Dobrynin et al., 1981) and some

early estimates were not previously summarized (e.g., Trofimuk et al., 1973, 1975, 1979; Cherskiy and Tsarev, 1977). In addition, two new global estimates of hydrate-bound gas in the ocean were presented recently (Soloviev, 2002; Milkov et al., 2003). A detailed historical analysis of the evolution of global gas hydrate estimates, as well as the approaches, assumptions and data used to produce them, appears necessary to better understand how much gas may actually be concentrated in gas submarine hydrate.

The objectives of the present study are to: (1) present an updated inventory of global estimates made over the last 30 years; (2) demonstrate how these estimates changed as a function of time and growing knowledge of gas hydrate distribution and concentration in marine sediments; and (3) assess the range of global estimates that would reflect the current understanding of gas hydrate. The significance of the presented data and conclusions for various speculations and models that consider the size of the global gas hydrate reservoir are discussed.

2. Review of global estimates in a chronological order

A list of 20 estimates of the global volume of hydrate-bound gas is presented in Table 2. Only original estimates (i.e., estimates that were not taken from previous works) are included. The widely cited estimate of Dobrynin et al. (1981) is not included in Table 2 because it was taken (and erroneously converted to cubic meters) from the work of Trofimuk et al. (1979). In the following analysis, I consider only the estimates in which the method of estimation is clearly presented and the parameters used in the calculations are estimated based on identified assumptions or direct measurements. There are 14 such estimates made in the period from 1973 to 2003, and they are described below and in Tables 2 and 3.

The possibility of gas hydrate formation in marine sediments was first considered in the USSR (Sokolov, 1966, cited in Milton, 1977), and Soviet geologists A.A. Trofimuk, N.V. Cherskiy and V.P. Tsarev were the first ones to estimate the distribution and the volume of submarine gas hydrate. Although Trofimuk et al. (1973) did not calculate the global volume of

Table 1
Global estimates of methane in submarine gas hydrate ($\times 10^{15}$ m³) (after Kvenvolden, 1999)

High–low value	Best estimate	Reference
5–25		Trofimuk et al. (1977)
	7600	Dobrynin et al. (1981)
	3.1	McIver (1981)
	40	Kvenvolden and Claypool (1988)
	10	Makogon (1981)
	21	Kvenvolden (1988)
	21	MacDonald (1990)
26–140	26	Gornitz and Fung (1994)
23–91	46	Harvey and Huang (1995)
	1	Ginsburg and Soloviev (1995)
	7	Holbrook et al. (1996)
	15	Makogon (1997)
2–20		Dickens et al. (1997)

Table 2

Revised inventory of global estimates of methane in submarine gas hydrate ($\times 10^{15}$ m^3)

High–low value	Best or average value	Reference
3021–3085	*3053*	***Trofimuk et al. (1973)***
	1135	**Trofimuk et al. (1975)**
	1573	**Cherskiy and Tsarev (1977)**
	~ 1550	Nesterov and Salmanov (1981)
	>0.016	Trofimuk et al. (1977)
~ 110–130	*~ 120*	***Trofimuk et al. (1979)***
	3.1	McIver (1981)
5–25	15	Makogon (1981), Trofimuk et al. (1981, 1983a)
	15	Trofimuk et al. (1983b)
	40	**Kvenvolden and Claypool (1988)**
	~ 20	**Kvenvolden (1988)**
	20	**MacDonald (1990)**
26.4–139.1	**26.4**	**Gornitz and Fung (1994)**
~ 22.7–90.7	~ 45.4	**Harvey and Huang (1995)**
	1	**Ginsburg and Soloviev (1995)**
	~ 6.8	*Holbrook et al. (1996)*
	15	Makogon (1997)
	>0.2	**Soloviev (2002)**
3–5	*4*	*Milkov et al. (2003)*
1–5	**2.5**	**This study**

Bold face denotes justified estimate used in the further analysis (see text for details) and italic face denotes the estimate that was calculated from the data presented by respective authors.

hydrate-bound gas, they presented data and assumptions that could be easily used to produce such an estimate. In their work, Trofimuk et al. (1973) assumed that gas hydrate (80% CH$_4$ and 20% CO$_2$) forms at water depths greater than 500 m and that this process occurs over 93% of the ocean's area. Using the average thickness of the gas hydrate occurrence zone (GHOZ, which in that study was assumed to be equal to the gas hydrate stability zone (GHSZ)) of 300 m and its areal extent (335.71 million km^2), they calculated the volume of rock within this zone (100.7 million km^3). They also assumed that sediments have an average porosity 20% and calculated that each cubic meter of sediment may contain from 30 to 36 m^3 of hydrate-bound gas (i.e., this is gas yield of hydrate-bearing sediments). The calculations obviously implied 100% gas hydrate saturation and gas hydrate yield 150–180 m^3. Based on the presented data and assumptions, the global volume of hydrate-bound gas may be calculated by multiplying the

global volume of the GHOZ and the gas yield of hydrate-bearing sediments (see Table 4 for the nomenclature):

$$V_{glob} = V_{GHZ} \times D \tag{1}$$

or

$$V_{glob} = A \times z \times \phi \times H \times G \tag{2}$$

The calculated global estimate of hydrate-bound gas thus is $(3021–3085) \times 10^{15}$ m^3.

Trofimuk et al. (1975) used an approach different from the one in their previous estimation. They assumed that gas (mainly methane) hydrate forms at depths exceeding 250 m in polar regions and 650 m in the tropics, and that the GHOZ occupies about 90% of the ocean floor. They determined the areal extent and thickness of the GHOZ separately for the shelf, continental slope and the abyssal plain (Table 3). Then, Trofimuk et al. (1975) considered a dynamic model that encompassed formation of gas hydrate in the GHOZ, decomposition upon burial, migration of gas back into the GHOZ and then recrystallization of the gas in gas hydrate. Based on this model, they estimated that from 1350 to 4000 m^3 of hydrate-bound methane must have accumulated per 1 m^2 of ocean floor (i.e., this is the gas hydrate resource density). Trofimuk et al. (1975) calculated the global volume of hydrate-bound methane (~ 1135×10^{15} m^3) as the sum of estimates for the shelf, continental slope and the abyssal plain:

$$V_{glob} = A \times R = (A \times R)_{shelf} + (A \times R)_{slope}$$
$$+ (A \times R)_{abyssal\ plane} \tag{3}$$

Cherskiy and Tsarev (1977) used a similar approach and many of the same assumptions (Table 3) as Trofimuk et al. (1975). However, they estimated a greater gas hydrate resource density (2077–5533 m^3/ m^2) and a greater gas yield of hydrate-bound sediments (10–80 m^3/m^3) below the seafloor. Cherskiy and Tsarev (1977) estimated the global volume of hydrate-bound methane at ~ 1573×10^{15} m^3. This estimate is adapted in the widely cited paper of Trofimuk et al. (1977), who state that "the total methane reserves of the world ocean are estimated to be more than 16×10^{12} m^3" (p. 923). There is no estimate of $(5–25) \times 10^{15}$ m^3 in the work of Trofimuk

Table 3
Main parameters used in the global estimations of hydrate-bound gas

Reference	Estimated zone	Estimated area of the GHSZ ($\times 10^6$ km²)	Hydrate-bearing area (A) ($\times 10^6$ km²)	Average thickness of GHZ (z) (m)	Volume of the GHSZ (V_{GHZ}) ($\times 10^6$ km³)	Volume of hydrate-bearing sediments (V_{GHSZ}) ($\times 10^6$ km³)	Porosity ϕ	TOC content (%)	Hydrate saturation (H) (%)	Gas hydrate yield (G) (m³/m³)	Gas yield of hydrate-bearing sediments (D) (m³/m³)	Gas hydrate resource density (R) (m³/m²)
Trofimuk et al. (1973)	World ocean	335.71	335.71	300	100.7	100.7	0.2		*100*	150–180	30–36	*900–920*
Trofimuk et al. (1975)	Shelf	26.7	2.6	60	*0.16*	0.16		0.7			24	1460
	Slope	76.5	76.5	200	*15.3*	15.3		1.3			6.7	1350
	Abyssal plane	257	257	300	*77.1*	77.1		0.3			13	4000
Cherskiy and Tsarev (1977)	Shelf	26.7	2.6	60	*0.16*	0.16					10–80	4842
	Slope	76.5	76.5	200	*15.3*	15.3						2075
	Abyssal plane	257	257	300	*77.1*	77.1						5533
Trofimuk et al. (1979)	Shelf	31.1	1	<300	*75.7*	28.2					30–36	1170–1384
	Slope	60.4	36.2									
	Abyssal plane	189	56.7									
McIver (1981)	*World ocean*					20.5		0.5			0.15	
Kvenvolden and Claypool (1988)	Sediments with >1% TOC	10	*10*	500	5	*5*	0.5	>1	10	160	*8*	*4000*
Kvenvolden (1988)	Slope	*14*	10.5	400 (40)	*5.6*	0.42	0.3		100	140	*42*	*1900*
MacDonald (1990)	Water depth 200–3000 m	62.4	*6.2*	500	31.2	*3.1*	0.4	1	10	156	*6.2*	*3200*
Gornitz and Fung (1994)	In situ bacterial accumulations	13.3–31.7	13.3–31.7	379.1–440	*5–13.9*	5–13.9	0.46	0.5–1	5–10	170	*5.2–10*	*2000–4400*
	Fluid migration areas	23	23	453.4	*10.4*	10.4	0.46		0–50	170	*11*	*5000*
Harvey and Huang (1995)	Water depth < 3000 m	*59.6*	14.8	277	16.5	*4.1*	<0.6	>0.5	2.5–10, 5–20, 10–40	170.7	*5.5–21.9*	*1500–6100*
Ginsburg and Soloviev (1995)	"Deep-seated" accumulations	40	*0.24*			*~ 0.1*					*3.2*	2000
	Seepage-associated areas		*0.04*			*~ 0.002*					*30*	1500
Holbrook et al. (1996)	Continental slope		*10.5*			*4.2*					1.9	*800*
Soloviev (2002)	Areas with >2 km sediments	35.7	*0.28*			*~ 0.1*					*0.7–3.1*	650
Milkov et al. (2003)	Continental margins				7	*2.1*					1.4–2.4	*160–800*
This study	Continental margins				7	*0.7–2*					1.4–2.4	*160–800*

Italic face denotes the values that were calculated from data presented by respective authors.

Table 4
Nomenclature of parameters used in Eqs. (1)–(3)

V_{glob}	global volume of hydrate-bound gas (m^3 at STP)
A	area of hydrate-bearing sediments (m^2)
z	thickness of the gas hydrate occurrence zone (m)
V_{GHZ}	volume of hydrate-bearing sediments (m^3)
ϕ	porosity (%)
H	gas hydrate concentration in pore space (%)
G	gas hydrate yield (volume of gas (at STP) per cubic meter of pure gas hydrate) (m^3/m^3)
D	gas yield of hydrate-bearing sediments (volume of hydrate-bound gas (at STP) per cubic meter of hydrate-bearing sediments) (m^3/m^3)
R	gas hydrate resource density (volume of hydrate-bound gas (at STP) per square meter of hydrate-bearing area) (m^3/m^2)

et al. (1977) although this range is cited by the Potential Gas Committee (1981) and is adapted by Kvenvolden (1988, 1999) and others. The estimate of $(5-25) \times 10^{15}$ m^3 was later presented by Trofimuk et al. (1981, 1983a) and Makogon (1981), but it was not properly justified and therefore is not discussed here.

Trofimuk et al. (1979) assumed that the appropriate pressure and temperature (*PT*) conditions for gas hydrate formation occur on 10% of the shelves, and that gas hydrate accumulates only in 33% of that area. They further suggested that although *PT* conditions favorable for gas hydrate formation occur in 100% of the area on continental slopes and the abyssal plain, gas hydrate accumulates only in 60% of the slope and 30% of the abyssal plain (Table 3). Trofimuk et al. (1979) assumed the thickness of the GHOZ to be 300 m and the gas hydrate resource density $1170-1384$ m^3/m^2. Using these assumptions and Eq. (3), the global volume of the hydrate-bound methane can be calculated as $\sim (110-130) \times 10^{15}$ m^3. However, Trofimuk et al. (1979) suggested that only 70% of methane may be extracted from gas hydrate and gave 85×10^{15} m^3 as the global volume of extractable hydrate-bound methane. Since the original estimate presented by Trofimuk et al. (1979) (85×10^{15} m^3) was an average estimate of gas hydrate reserves rather than the volume of hydrate-bound methane, the calculated values (($110-130) \times 10^{15}$ m^3) are listed in Table 2 and will be used in the following analysis. The widely cited estimate by Dobrynin et al. (1981) was adapted from the work of Trofimuk et al. (1979).

McIver (1981) presented the first western estimate of the global volume of hydrate-bound methane. He

calculated that, if the average organic carbon content of sediment is 0.5%, and that only 1% of that organic carbon is converted to methane by microbial action, then the gas yield of hydrate-bound sediments would be 2.2×10^{10} ft^3 of gas per cubic mile of sediment (i.e., 0.15 m^3/m^3). Then, McIver (1981) extrapolated this gas yield to "the sediment volume of the world" (p. 721) and estimated the global volume of hydrate-bound methane (in accordance with Eq. (3)) of 110,000 tcf (3.1×10^{15} m^3).

Kvenvolden and Claypool (1988) assumed that gas hydrate forms only from methane generated in situ. They concluded that sediments should contain 2% of total organic carbon (TOC) at the depth of the onset of methanogenesis and 1% TOC at the depth of the base of the GHSZ to generate 10% gas hydrate saturation in 50% porosity. Thus, they considered only sediments containing >1% TOC and estimated their areal extent to be about 10×10^6 km^2. Assuming the average thickness of the GHSZ (0.5 km) and the average porosity of sediments in the GHSZ (50%), 10% gas hydrate saturation in pores and gas hydrate yield 160 m^3, Kvenvolden and Claypool (1988) used Eq. (2) to calculate the global volume of hydrate-bound methane at 40×10^{15} m^3.

Kvenvolden (1988) presented an estimate that appears to be the most widely-cited at present. The global estimate is an extrapolation from the estimate made for the Arctic Ocean by Kvenvolden and Grantz (1990). Based on the regional seismic studies of the Bottom Simulating Reflector (BSR, a reflector commonly believed to be associated with gas hydrate), it was assumed that gas hydrate in the Arctic Ocean is present over 75% of the area at water depth $400-2800$ m. Average thickness of the GHSZ was estimated at 400 m, but it was concluded that gas hydrate may be present only in the 40-m-thick layer (i.e., the GHOZ) above the BSR. Further assuming average porosity of 30%, gas hydrate saturation 100% and gas hydrate yield 140 m^3, Kvenvolden and Grantz (1990) calculated (using Eq. (2)) that 8.8×10^{14} m^3 (or $\sim 10^{15}$ m^3) of methane is concentrated in the Arctic Ocean gas hydrate. Kvenvolden (1988) estimated that the Arctic Basin margin comprises $\sim 5\%$ of the total length of continental margins worldwide. Assuming that the submarine gas hydrates occur in the other areas in concentrations similar to those in the Arctic, Kvenvolden calculated the global amount of methane carbon in

gas hydrates to be ~ 11,000 Gt (~ 20×10^{15} m^3 of methane).

MacDonald (1990) made a series of assumptions (Table 3) and estimated that the total pore space available for gas hydrate formation at the continental margins is 12.5×10^6 km^3. Assuming that only 10% of the available pore space of sediment within the GHSZ actually contains gas hydrate with 10% gas hydrate saturation, MacDonald (1990) obtained (in accordance with Eq. (2)) a global estimate of hydrate-bound methane at 20×10^{15} m^3.

Gornitz and Fung (1994) considered two different models of gas hydrate accumulation in sediments. In the ''in situ bacterial generation'' model, they assumed that gas hydrate forms in sediments containing more than 0.5% TOC. The areal extent of such sediments was obtained from the distribution of photosynthetically active biomass as given by the annual average coastal zone color scanner. Other parameters assumed are listed in Table 3. The volume of hydrate-bound methane was estimated (using Eq. (2)) to be $(26.4–139.1) \times 10^{15}$ m^3. In the ''fluid migration'' model, Gornitz and Fung (1994) implied that gas hydrate forms only in the areas of active fluid migration in sediments, and gas hydrate saturation in sediments linearly decreases from 50% of pores at the base of the GHSZ to 0% at the top of the GHSZ. In this model (see Table 3 for other parameters), the global volume of hydrate-bound methane is estimated to be 114.5×10^{15} m^3. Gornitz and Fung (1994) further stated that the most likely (best guess) value is on the lower end of the estimated range, i.e., 26.4×10^{15} m^3.

Harvey and Huang (1995) assumed that gas hydrates accumulate within 75% of the area with sediments containing >0.5% TOC. They further considered three distributions of gas hydrate saturation in the range 2.5–40% of porosity (see Table 3 for other parameters) and used Eq. (2) to estimate the global amount of hydrate-bound methane carbon at 12,200, 24,400 and 48,800 Gt. These correspond to (22.7, 45.4 and 90.7) $\times 10^{15}$ m^3 of methane, respectively. Harvey and Huang (1995) further stated that the most likely (best guess) value is 24,400 Gt of methane carbon.

Ginsburg and Soloviev (1995) considered two types of gas hydrate accumulations, namely (1) associated with hydrocarbon seepage at the seafloor and (2) deep-seated, or not directly associated with seepage at the seafloor. They assumed that seafloor seeps

with gas hydrates in sediments occur over 0.01% of the area of continental slopes (i.e., 4×10^4 km^2) and that the gas hydrate resource density at seep sites is similar to those observed at the Buzdag mud volcano in the Caspian Sea (1500 m^3/m^2). Using Eq. (3), Ginsburg and Soloviev (1995) estimated the volume of hydrate-bound gas associated with seafloor seeps at 6×10^{13} m^3. For deep-seated accumulations, they analyzed drilling results from the DSDP Site 570 in the Middle America Trench where ~ 4-m-thick gas hydrate layer was observed and partially sampled (Kvenvolden and McDonald, 1985). Ginsburg and Soloviev (1995) calculated that the gas hydrate resource density at this Site may be as high as 2000 m^3/m^2. Then, they assumed that since Site 570 was one of 170 sites drilled on continental margins, similar gas hydrate accumulations may occur in 1/170 (0.6%) of continental margins (i.e., 24×10^4 km^2). Ginsburg and Soloviev (1995) used Eq. (3) to estimate that the global volume of hydrate-bound gas should be comparable to 4.8×10^{14} m^3 and suggested that it is approximately equal to 10^{15} m^3.

Holbrook et al. (1996) studied seismic velocities on the Blake Ridge during ODP Leg 164 and estimated that the average gas hydrate concentration in that area is ~ 5% of porosity. They did not extrapolate their results for all continental margins and did not give a global estimate of hydrate-bound gas, but suggested that the current global estimates of methane stored in hydrates (as presented in Kvenvolden, 1988) may be too high by as much as a factor of 3. Thus, it is appropriate to calculate a global estimate by reducing Kvenvolden (1988) estimate (~ 11,000 Gt of methane carbon) by a factor of 3 to ~ 3700 Gt of carbon or ~ 6.8×10^{15} m^3 of methane.

Soloviev (2002) used an approach similar to that of Ginsburg and Soloviev (1995) but he refined the assumptions based on a larger dataset. He assumed that gas hydrate may form only in the areas where the sedimentary cover is thicker than 2 km and estimated that such areas cover 35.7×10^6 km^2. Then, Soloviev (2002) considered gas hydrate distribution and concentration in specific gas hydrate accumulations (based on published DSDP/ODP drilling and shallow coring results) and concluded that the average gas hydrate resource density in the studied areas is ~ 650 m^3/m^2. Soloviev (2002) further suggested that gas hydrate accumulations are distributed in nature similarly to

conventional gas accumulations (for which gas resource density in individual fields is ~ 130 times less than that in megaprovinces) and thus the average gas hydrate resource density within all potential hydrate-bearing areas in the ocean (i.e., areas with >2-km-thick sedimentary cover) should not exceed 5 m^3/m^2. He estimated (using Eq. (3)) that the global volume of hydrate-bound gas (mainly methane) may be as low as 1.8×10^{14} m^3, or roughly 0.2×10^{15} m^3. Soloviev (2002) further stated that this value should be considered as minimal possible estimate.

Milkov et al. (2003) used direct measurements of methane concentration in sediments obtained through the deployment of Pressure Core Sampler (PCS) on Hydrate Ridge during ODP Leg 204. They estimated that the average gas hydrate concentration in the large study area characterized by a strong BSR but low gas flux to the seafloor may not exceed ~ 1% of pores in the GHSZ (~ 2% of pores in the GHOZ). They used the PCS results from the Hydrate Ridge and a comparable set of direct measurements of methane concentration from the Blake Ridge (Dickens et al., 1997) to estimate that sediments in the GHSZ in areas with the BSR but without seafloor seepage may yield on average only 1.4–2.4 m^3/m^3 of hydrate-bound methane. In their calculations (in accordance with Eq. (1)), Milkov et al. (2003) further assumed that the global volume of the GHSZ in continental margins is about 7×10^6 km^3 (Dickens, 2001a) and that only ~ 30% of continental margins contain gas hydrate (Borowski et al., 1999). Their global estimate of hydrate-bound methane is $(3–5) \times 10^{15}$ m^3.

3. Discussion

3.1. Decrease of global estimates as a function of time and the growing understanding of natural gas hydrate

The well-justified global estimates of hydrate-bound gas in the marine sediments described above are plotted in Fig. 1a as a function of year in which the estimate was made. It appears that the global estimates consistently decreased from 1970s to present. The difference between the earliest and the latest estimates is very significant (3–4 orders of magnitude). The negative correlation between the estimated volumes of hydrate-bound gas and the number of published

research papers on gas hydrate (Fig. 1) suggests that global estimates decreased as the understanding of natural gas hydrate in marine sediments increased. This may also be demonstrated through the comparison of the approaches and assumptions used to produce the global estimates. Three periods in which similar approaches and assumptions were applied to estimate
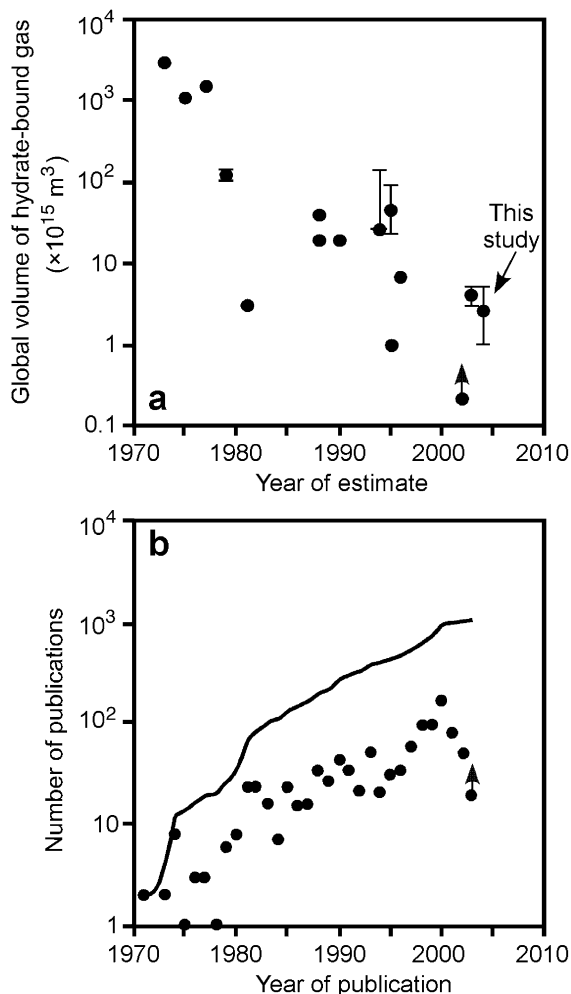

Fig. 1. (a) Global estimates of the volume of hydrate-bound gas in marine sediments versus the year in which the estimate was made (based on data in Table 2). Only the well-justified estimates are shown. Dots indicate the average or best value and bars indicate the range of estimates as given by authors or calculated in this study. (b) Number of publications with words "gas (methane) hydrate(s)" in titles. Dots show the number of publications in a given year, and line shows the cumulative number of publications. Data from the major GeoRef® database.

the global gas hydrate inventory can be distinguished: (1) 1970s–early 1980s (pre-mapping and pre-drilling estimates); (2) late 1980s–early 1990s (pre-drilling estimates); and (3) late 1990s–present (estimates based on drilling results). The global estimates decreased by at least one order of magnitude at transitions from one period to another.

The first estimates were produced in 1970s and early 1980s [from Trofimuk et al. (1973) to McIver (1981)], when the distribution and concentration of gas hydrate in marine sediments were largely unknown and only limited samples were recovered (see Ginsburg and Soloviev, 1998 for review). Trofimuk et al. (1973) assumed that gas hydrates composed of methane and CO_2 occur over 93% of the ocean and occupy 100% porosity in sediments (Table 3, Fig. 2). In the later work, Trofimuk et al. (1979) accepted that only a portion of the ocean floor may contain gas (mainly methane) hydrate. However, their estimate included large areas of the abyssal plain from which little (if any) evidence of gas hydrate has been reported at present. In addition to the large hydrate-bearing areas, high gas yield of hydrate-bearing sediments (as a result of high (up to 100%) gas hydrate saturation) was commonly assumed in the early studies (Table 3, Fig. 2). Consequently, the early estimates were very high, on the order

Fig. 3. Estimates and measurements of gas yield of hydrate-bearing sediments versus the year in which the estimate or measurements were made (based on data in Table 3). Dots indicate the average or best value and bars indicate the range of estimates and measurements as given by authors or calculated in this study.

of 10^{17}–10^{18} m^3 of methane. The estimate of McIver (1981) is an obvious exception from the range of estimates in that period. Although a quite extensive hydrate-bearing area was assumed in his estimate, McIver (1981) assumed a very low gas yield of hydrate-bearing sediments (Table 3, Figs. 2 and 3). He estimated that parameter at 0.15 m^3/m^3, which is two orders of magnitude lower than was assumed by others. Moreover, 0.15 m^3/m^3 is an order of magnitude lower than the average values recently measured in the hydrate-bearing sediments on divergent (Dickens et al., 1997) and convergent (Milkov et al., 2003) continental margins. The overestimated area of hydrate-bearing sediments and underestimated gas yield of sediments fortunately canceled, and the estimate of McIver (1981) approaches some recent estimates.

The estimates produced in late 1980s and early 1990s [from Kvenvolden and Claypool (1988) to Harvey and Huang (1995)] were apparently based on the concept that gas hydrate does not occur everywhere in the ocean but is rather concentrated along continental margins. This concept relied on first inventories and maps of gas hydrate distribution in the ocean (Kvenvolden and Barnard, 1983) and the assumption that sediments should contain a certain amount of organic carbon necessary to generate enough methane for gas
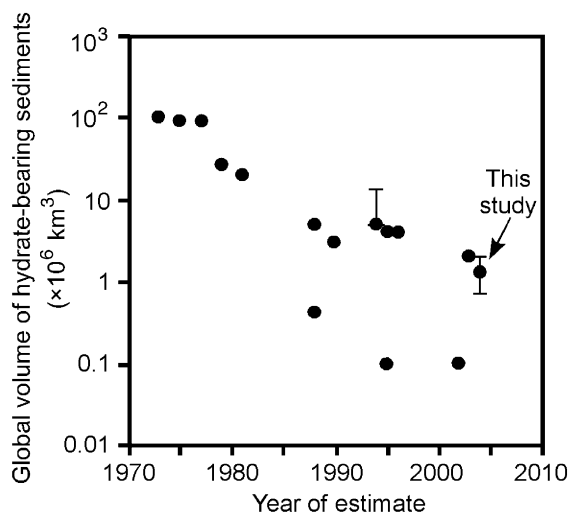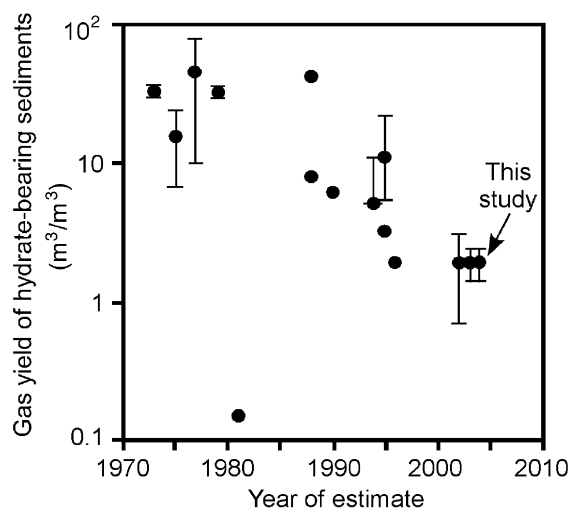

Fig. 2. Estimates of global volume of hydrate-bearing marine sediments versus the year in which the estimate was made (based on data in Table 3). Dots indicate the average or best value and bars indicate the range of estimates as given by authors or calculated in this study.

hydrate crystallization. Thus, most studies delineated the potential hydrate-bearing areas based on the assumed threshold of TOC in sediments (usually >0.5% or >1%, Table 3). Moreover, some studies considered that gas hydrates could occupy only a portion of the continental margins (e.g., 10% in the study by Mac-Donald, 1990 and 75% in the work of Kvenvolden, 1988). The gas hydrate concentration in sediments was assumed in that period mainly based on seismic data (e.g., Lee et al., 1994). Although gas hydrate samples were recovered at several DSDP and ODP Sites (see review by Ginsburg and Soloviev, 1998), reliable methods to estimate gas hydrate concentration in sediments were rarely used. Various studies assumed a range of gas hydrate concentration in sediments (from 0–50% (Gornitz and Fung, 1994) to 100% (Kvenvolden, 1988)), but it was generally accepted that gas hydrates do not occupy all pore space everywhere in the GHSZ. The calculated gas yield of hydrate-bearing sediments implied in that period varies from 5.2 to 42 m^3/m^3 (Table 3, Fig. 3). The growing knowledge of gas hydrate distribution and concentration in sediments lead to the set of estimates on the order of 10^{16} m^3 of methane, i.e., one or two orders of magnitude lower that the estimates in the previous period. Moreover, the produced estimates were relatively close to each other and two of them (Kvenvolden, 1988; MacDonald, 1990) coincided. This allowed Kvenvolden (1999) to propose the widely used ''consensus'' global estimate of hydrate-bound methane ($\sim 21 \times 10^{15}$ m^3).

The most recent estimates (starting with Ginsburg and Soloviev, 1995) are based on direct and indirect data obtained during DSDP and ODP drilling and data from drop cores. These data were used to constrain the areal extent of hydrate-bearing sediments, their gas yield or both. Although a relatively well-constrained low gas yield of hydrate-bearing sediments was used in the estimate of Holbrook et al. (1996) based on measurements of seismic velocities, those authors apparently adapted the assumption of Kvenvolden (1988) that gas hydrate accumulates over 75% of continental margins. In the other estimates produced in this period, the hydrate-bearing area was constrained based on the drilling results. Ginsburg and Soloviev (1995) argued that relatively large gas hydrate accumulations with volume of methane similar to that at Site 570 may occupy <1% of continental margins (similar assumption was made by Soloviev, 2002). Milkov et al. (2003)

conservatively assumed, based on a global study of the depth of the sulfate–methane interface at DSDP/ODP Sites (Borowski et al., 1999), that gas hydrates accumulate over $\sim$ 30% of the continental margins. The gas yield of hydrate-bound sediments was constrained by indirect (Holbrook et al., 1996) and direct (Milkov et al., 2003) measurements or was calculated based on published data on gas hydrate distribution and concentration at drilled Sites (Ginsburg and Soloviev, 1995; Soloviev, 2002). The estimates of the gas yield of sediments fall in a relatively narrow range 0.7–3.1 m^3/m^3 (i.e., average gas hydrate saturation $\sim$ 0.4–2 vol.%), and the direct measurements indicate the range 1.4–2.4 m^3/m^3 (Table 3, Fig. 3). Because of lower estimates of the hydrate-bearing area (Fig. 2) and the gas yield of hydrate-bearing sediments (Fig. 3), the most recent studies place the global volume of hydrate-bound methane at $10^{14}–10^{15}$ m^3, i.e., one or two orders of magnitude lower that the estimates in the previous period.

3.2. How much is really out there?

It is established above that the previous global estimates of hydrate-bound gas decreased as the knowledge of natural gas hydrate in marine sediments increased. However, does that mean that the estimates will continue decreasing in the future as more data becomes available? I suggest that this is unlikely because the main assumptions on which the most recent estimates are based were relatively well constrained by direct sampling of gas hydrate accumulations.

A simple volumetric method has been used in all studies discussed above. The volume of the GHSZ in the areas where gas hydrate is likely to accumulate is one parameter needed in this method. The most recent studies place this parameter at $\sim (0.1–2) \times 10^6$ km^3. Since the average thickness of the GHSZ is commonly assumed to be $\sim$ 300–500 m (Table 3), the estimated volume of hydrate-bearing sediments largely depends on the assumed hydrate-bearing area. Constraining the hydrate-bearing area based on the TOC content of sediments (a common technique in the late 1980s and early 1990s) may not be a reasonable approach because the TOC content may vary significantly through depth and the values measured in shallow sediments may provide little information on the generation potential of deeper sediments (G. Dickens, personal communication, 2003). In addition, migration of gas

from deep sediments into the GHSZ plays an important role in the formation of many gas hydrate accumulations not necessarily associated with high gas flux at the seafloor (Hovland et al., 1997; Xu and Ruppel, 1999; Milkov and Sassen, 2002). The hydrate-bearing area is best estimated from direct or indirect evidence of gas hydrate in sediments. Samples of gas hydrate have been recovered from ~ 3.5% of DSDP and ODP Sites drilled on continental margins (Borowski et al., 1999). Detailed pre-Leg site surveys indicated that a BSR was present at or near ~ 8.5% sites (Borowski et al., 1999). Taking into account that potential hydrate-bearing areas with a BSR were often purposely avoided during early DSDP and ODP drilling activities (Hovland et al., 1999), it seems prudent to suggest that hydrate-bearing sediments occupy perhaps at least 10% of continental margins. The upper limit for this parameter may be placed at 30% of continental margins as suggested by the study of sulfate–methane interface at drilled Sites (Borowski et al., 1999). Thus, the volume of hydrate-bearing sediments taken as 10–30% of the volume of the GHSZ on continental margins (Dickens, 2001a) is likely to be in the range $(0.7-2) \times 10^6$ km^3 (Fig. 2).

The gas yield of hydrate-bearing sediments is the other parameter needed to estimate the volume of hydrate-bound gas by the volumetric method. In the early estimations, this parameter was implied to be relatively high based on the assumption of significant gas hydrate saturation in the pore space (Table 3, Fig. 3). However, the gas yield of sediments in hydrate-bearing areas with a strong BSR has been recently constrained by direct measurements on the Blake Ridge (Dickens et al., 1997) and Hydrate Ridge (Milkov et al., 2003). The measurements indicate that sediments in the GHSZ contain on average only ~ 1.4–2.4 m^3/m^3 of hydrate-bound methane (i.e., gas hydrate saturation ~ 0.9–1.5 vol.%). The intervals with gas hydrate may contain more methane than the average values, but they are leveraged by hydrate-free sediments mainly in the upper part of the GHSZ near the seafloor.

If the presented above ranges of the global volume of the GHSZ and the gas yield of hydrate-bearing sediments properly reflect the current knowledge of gas hydrate distribution and concentration in sediments, then the global volume of hydrate-bound gas is (in accordance with Eq. (3)) in the range (1–

5) $\times 10^{15}$ m^3 of methane (~ 500–2500 Gt of methane carbon). To further constrain this estimate, additional studies are needed to better determine the global distribution of gas hydrate in marine sediments and to measure gas concentration in the GHSZ in various geologic environments. However, it seems unlikely that future global estimates will be significantly different from the range presented above since the main parameters used in this estimation are constrained relatively well by DSDP/ODP drilling.

The global estimate presented above does not include structural gas hydrate accumulations (see Milkov and Sassen, 2002 for geological classification of gas hydrate accumulations) directly associated with geologic structures such as faults and mud volcanoes that facilitate high gas flux at the seafloor. These accumulations may contain very significant gas hydrate concentrations (Hovland et al., 1997; Milkov and Sassen, 2002). For example, sediments at the recently drilled structural accumulation at the southern summit of Hydrate Ridge offshore Oregon have an average gas hydrate concentration ~ 11% of pores (average gas yield ~ 13.5 m^3/m^3) and some intervals contain up to 43 vol.% of gas hydrate (gas yield >50 m^3/m^3) (Milkov et al., 2003). However, the global area and the volume of hydrate-bearing sediments at structural accumulations may be insignificant. Ginsburg and Soloviev (1995) suggested that those accumulations occupy only 0.01% of continental margins and may contain 0.002×10^6 km^3 of hydrate-bearing sediments. These authors further suggested that, on a global scale, gas hydrate accumulations associated with seafloor seeps contain one order of magnitude less hydrate-bound gas than the accumulations not associated with high gas flux to the seafloor. Soloviev (2002) estimated that individual accumulations associated with gas seepage in the Norwegian, Caspian, Mediterranean and Okhotsk seas contain 10^8-10^9 m^3 of gas at STP. Milkov and Sassen (2003b) provided a preliminary assessment of gas hydrate resources at seven structural accumulations in the Gulf of Mexico and suggested that they may contain from 4.7×10^8 to 1.3×10^{11} m^3 of gas in place. Milkov et al. (2003) estimated that the gas hydrate accumulation at the southern summit of Hydrate Ridge associated with high gas flux at the seafloor contains ~ 3×10^8 m^3 of methane. Thus, from 10^4 large to 10^7 small structural gas hydrate

accumulations may be needed so these accumulations could contribute significantly to the global volume of hydrate-bound gas. It is well established that structural gas hydrate accumulations occur worldwide both on convergent and divergent margins (Ginsburg and Soloviev, 1998; Milkov and Sassen, 2002), but additional analysis of their distribution and further ocean exploration is required to better constrain the total number of such accumulations.

It may be educational to compare the global estimates with some well-justified regional estimates of hydrate-bound gas (G. Dickens, 2002, personal communication). Dickens et al. (1997) estimated that 15 Gt of methane carbon is stored in gas hydrates over 26,000 km^2 of the Blake Ridge. Milkov and Sassen (2001) suggested that ～5–8 Gt of carbon may be present in gas hydrates of the Gulf of Mexico (these gas hydrates may contain significant volumes of C_{2+} hydrocarbon gases). Thus, ～650 areas similar in size and gas hydrate concentration to the Blake Ridge (or ～1250–2000 areas similar to the Gulf of Mexico) should exist in the ocean to account for 10,000 Gt of carbon in the global gas hydrate inventory as suggested by Kvenvolden and Lorenson (2001). This seems highly unrealistic. Approximately 170 areas similar to the Blake Ridge (～300–500 areas similar to the Gulf of Mexico) are needed to account for the upper limit of the global gas hydrate inventory proposed in this study (2500 Gt), which, although more probable, still may be unrealistic.

4. Implications

4.1. Gas hydrate as a component of the global carbon cycle

Several recent studies emphasized that gas hydrate may be an important component of the global carbon

cycle (Kvenvolden, 2002; Dickens, 2001b). This conclusion was largely based on the assumption that the gas hydrate reservoir of methane carbon is "enormous when compared to the sizes of the other organic carbon reservoirs" (Kvenvolden, 2002, p. 302). The comparison of various reservoirs of organic carbon in the Earth (Fig. 4) indeed suggests that the global gas
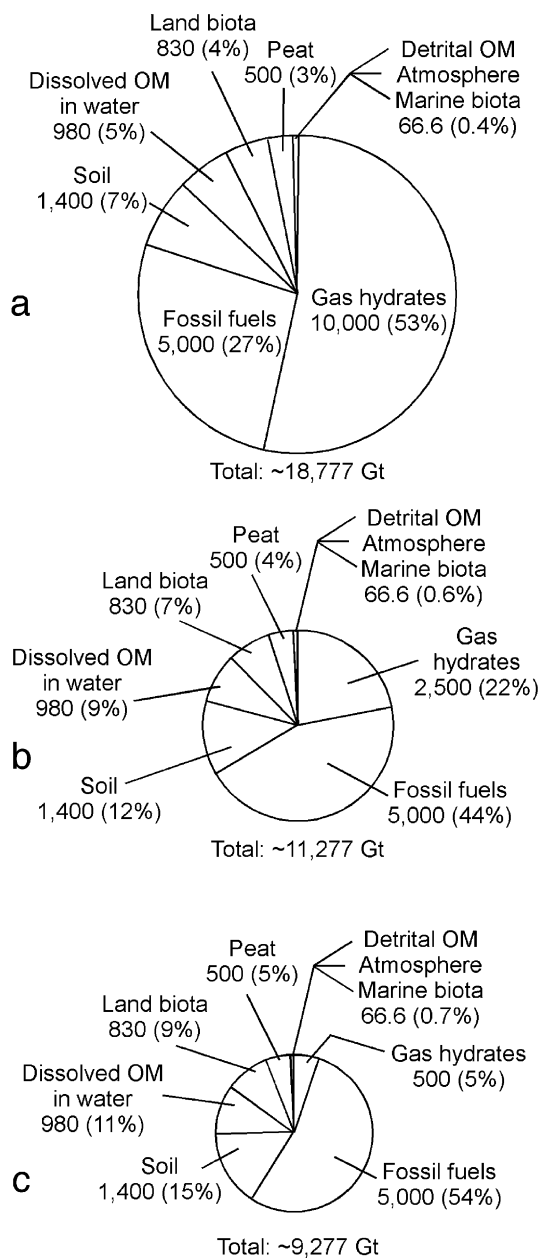

Fig. 4. Distribution of organic carbon in the Earth (excluding dispersed organic carbon such as kerogen and bitumen) with varying estimates of the global hydrate inventory. Values are given in Gt of carbon. (a) The distribution based on the estimate of 10 000 Gt of methane carbon in gas hydrates (Kvenvolden, 1993). (b) The distribution based on the revised estimate of the global gas hydrate inventory assuming the global volume of hydrate-bound gas at upper bound. (c) The distribution based on the revised estimate of the global gas hydrate inventory assuming the global volume of hydrate-bound gas at lower bound.

hydrate inventory contains more carbon than all other reservoirs (excluding dispersed organic carbon such as kerogen and bitumen) combined, but only if its size is set at 10,000 Gt of methane carbon. However, if the global gas hydrate inventory is only 500–2500 Gt of methane carbon as suggested in the present study, then the size of the gas hydrate reservoir, although large, is comparable to other reservoirs such as soil or dissolved organic matter in water (Fig. 4).

Milkov et al. (2003) used their global estimate of hydrate-bound methane to demonstrate that a significantly smaller global hydrate reservoir creates a fundamental problem for paleoceanographic scenarios relying on rapid release of methane from decomposed gas hydrate to the ocean and atmosphere (Dickens et al., 1995; Hesselbo et al., 2000; Jahren et al., 2001). Dickens et al. (1995) proposed that the $-2‰$ to $-3‰$ excursion in the $\delta^{13}C$ of global carbonate across the Paleocene–Eocene Thermal Maximum time interval (PETM, ~ 55 Ma) was caused by gas hydrate decomposition. At least 1200–2300 Gt of methane carbon would be required to cause the observed $\delta^{13}C$ excursion (Dickens et al., 1995). The global volume of the Paleocene GHSZ has been estimated to be $\sim 43\%$ of the present GHSZ (due to higher bottom water temperature) and decreased by $\sim 53\%$ during the PETM (Dickens, 2001a). If the Paleocene GHSZ had the same gas yield per volume of hydrate-bearing sediments as estimated for the present GHSZ, then maximum ~ 600 Gt of methane carbon could have been released from decomposed gas hydrate. Most of the released gas likely would have been sequestered and consumed in the remaining GHSZ (Milkov and Sassen, 2003a), and only a small portion (less than $\sim 21\%$ (Dickens, 2001a) or < 130 Gt of methane carbon) would have escaped into the ocean and affected its carbon pool. Therefore, the amount of methane released during the PETM would have been at least an order of magnitude lower than the amount needed to cause the observed isotopic excursion. Milkov et al. (2003) concluded that either sediments in the past contained significantly more gas hydrates (or free gas), or other carbon sources need to be invoked to explain the sudden input of a massive quantity of ^{13}C-depleted carbon (Kent et al., 2003). Similar conclusions were made by Milkov and Sassen (2003a), who modeled gas hydrate decomposition in response to regional bottom water temperature

increases and drops in sea level in the Gulf of Mexico. They estimated that hydrocarbon gases may be released from decomposed gas hydrate at a rate considerably lower than the gas seepage from a leaky subsurface petroleum system and suggested that the role of gas hydrate in global change is likely to be overestimated.

4.2. Gas hydrate as a potential energy source

It is commonly believed that gas hydrate is a potential energy source because the amount of methane carbon in gas hydrates is twice as large as the carbon present in other fossil fuel deposits (coal, oil, natural gas) (Fig. 4; Kvenvolden, 1993, Collett, 2002). However, if the global amount of methane carbon in gas hydrate is 500–2500 Gt as suggested in the present study, this statement is not likely to be valid (especially if greater estimates of fossil fuel carbon (e.g., 16,000 Gt of Hunt, 1972) are considered). However, even the updated estimate suggests that the global gas hydrate inventory may contain a very significant volume of gas. The global volume of hydrate-bound gas may be 2–10 times greater than the global conventional gas endowment that includes undiscovered gas resources, reserve growth, remaining reserves and cumulative production $(0.436 \times 10^{15} \ m^3$, USGS World Energy Assessment Team, 2000).

However, the knowledge of the global volume of hydrate-bound gas is not greatly important in the considerations of gas hydrate as a future energy resource. The global volume represents the ultimate geologic resource of hydrate-bound gas, and many additional considerations, not necessarily geological, define what part of these resources may become reserves (i.e., may be profitably recovered). Milkov and Sassen (2002) emphasized that gas hydrate reserves are likely to represent only a small fraction of the gas hydrate resources because the largest volume of gas hydrate is in subeconomic stratigraphic accumulations similar to the one at the Blake Ridge. These inferences are consistent with the previous results of Hovland et al. (1997) who studied gas hydrates associated with BSRs on the Niger Delta front and concluded that gas hydrates are too dispersed to have commercial potential for recovering. However, some concentrated structural gas hydrate accumulations associated with fluid migration con-

duits in the subsurface and high gas flux at the seafloor may be exploited profitably (Hovland et al., 1997; Milkov and Sassen, 2002, 2003b).

The gas yield of hydrate-bearing sediments and the total volume of hydrate-bound gas are among the main geologic factors that define the economic potential of a gas hydrate accumulation. Direct measurements at the southern summit of Hydrate Ridge suggest that the gas yield of hydrate-bearing sediments at many structural accumulations may be as high as ~ 13.5 m^3/m^3 on average (Milkov et al., 2003). However, the volume of hydrate-bearing sediments is often too small to hold significant gas resources. A gas hydrate accumulation must contain a volume of gas comparable to the reserves in medium to large conventional gas fields to have economic potential. On this basis, many well-studied structural gas hydrate accumulations that contain relatively small volumes of gas are likely to be subeconomic (e.g., Håkon Mosby mud volcano in the Norwegian Sea (Ginsburg et al., 1999; Milkov and Sassen, 2002), Bush Hill (Green Canyon blocks 184 and 185) in the Gulf of Mexico (Milkov and Sassen, 2003a) and the southern summit of Hydrate Ridge offshore Oregon (Milkov et al., 2003)). However, large structural accumulations may provide marginal or economic reserves in the future. One such an accumulation occurs in the Mississippi Canyon blocks 852 and 853 in the Gulf of Mexico and may contain $1.1–2.3 \times 10^{10}$ m^3 or 0.4–0.8 tcf of gas (Milkov and Sassen, 2003b).

5. Conclusions

Global estimates of hydrate-bound gas in submarine environments have decreased over the last 30 years from $10^{18}–10^{17}$ to $10^{14}–10^{15}$ m^3 at STP as a result of growing knowledge of gas hydrate distribution and concentration in sediment. It appears that the widely cited and used "consensus value" of 21×10^{15} m^3 of methane (or $\sim 10,000$ Gt of methane carbon) may represent a consensus only for the estimates made in the late 1980s–early 1990s when most studies assumed that gas hydrates occur over large portion of continental margins and occupy approximately 10% of pores on average. The DSDP and especially ODP drilling results suggest that both the area of hydrate-bearing sediments and gas hy-

drate concentrations (or gas yield of sediments) were previously overestimated. It appears that the global volume of hydrate-bearing sediments may be in the range $(0.7–2) \times 10^6$ km^3, and one cubic meter of these sediments may contain less than 2.5 m^3 of hydrate-bound gas (i.e., < 1.6 vol.% of gas hydrate) on average. The global volume of hydrate-bound gas that best reflects the current knowledge of submarine gas hydrates is in the range $(1–5) \times 10^{15}$ m^3 of methane ($\sim 500–2500$ Gt of methane carbon), or from four to twenty times less than widely cited estimates. This suggests that although the gas hydrate inventory may be large, it may be comparable in size to other reservoirs of organic carbon such as soil and dissolved organic matter. The role of gas hydrate in global change may also be overestimated. It appears that mostly large concentrated gas hydrate accumulations usually associated with geological structures that facilitate the migration of fluids into the GHSZ may provide future exploitable gas reserves.

Acknowledgements

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