Modeling of methane bubbles released from large sea-floor area: Condition required for methane emission to the atmosphere

A. Yamamoto [a,*], Y. Yamanaka [a,b], E. Tajika [c]

[a] Graduate School of Environmental Science, Hokkaido University, Sapporo, 060-0810, Japan
[b] Frontier Research Center for Global Change, Japan Agency for Marine-Earth Science and Technology, Yokohama, 236-0001, Japan
[c] Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, Japan

ABSTRACT

Massive methane release from sea-floor sediments due to decomposition of methane hydrate, and thermal decomposition of organic matter by volcanic outgassing, is a potential contributor to global warming. However, the degree of global warming has not been estimated due to uncertainty over the proportion of methane flux from the sea-floor to reach the atmosphere. Massive methane release from a large sea-floor area would result in methane-saturated seawater, thus some methane would reach the atmosphere. In this study, we discussed the possibility of the methane release from a large sea-floor area to the atmosphere focusing on methane saturation in the water column necessary for a methane bubble to reach the atmosphere. Using a one-dimensional numerical model integrated over time, we predict methane bubbles and methane concentration in the water column under the condition of continuous methane input from the sea-floor to the water column. We found that some methane bubbles reach the atmosphere even when the methane saturation fraction in the water column is much lower than 100%. We compared the methane input from the sea-floor required for a methane bubble to reach the atmosphere to the amount of methane in the sediment in the form of methane hydrate and free gas. In most cases, our results suggest that the typical amount of methane in the sediment (i.e., typical hydrate fraction of ~2% and free gas of two-thirds of the amount of hydrate) is significantly lower than the required minimum methane input. It is, therefore, suggested that, except in the case of an extraordinary methane flux, the massive quantity of methane bubbles released from sea-floor gas hydrate would not reach the atmosphere directly but would be dissolved in the seawater. With regard to global warming due to human activities, the release of methane bubbles due to methane hydrate decomposition may not be enough to significantly accelerate total global warming. In the case of metamorphic methane release during PETM, there is the possibility that the released methane resulted in methane-saturated seawater, allowing some methane to reach the atmosphere.

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1. Introduction

A large amount of methane degassing from the sea-floor has the potential to impact the climate. Since Global Warming Potential of methane for 100-yr (20-yr) is 21 (72) times greater than that of CO_2 (IPCC, 2007), a methane discharge to the atmosphere should cause significant warming until the methane is oxidized to carbon dioxide on the time scale of approximately ten years (Prather et al., 2001). After oxidation to carbon dioxide, warming continues until the major portion of carbon dioxide is absorbed into the ocean (~thousands of years). On the other hand, methane dissolved in seawater is oxidized quickly to carbon dioxide in the ocean on the timescale of about one year (Valentine et al., 2001). A part of the dissolved carbon dioxide could be emitted to the atmosphere and cause a small contribution to warming. As for the impact after equilibration of partial pressure of carbon dioxide between atmosphere and ocean (after ~1000 years), the impact would be the same as in the case for methane release to the atmosphere, although the two impacts before the equilibration are drastically different from each other. Thus understanding the dynamics of vertical transport of methane gas in the ocean is crucial in order to evaluate the climate response to methane release from the sea-floor.

Methane-bubbling seep sites extending over an area of <1 km^2 have been found by visual and acoustic investigations. Almost all bubbles released from deep water can rise up hundreds of meters, but not reach the atmosphere (Heeschen et al., 2003; Matveeva et al., 2003; Greinert et al., 2006; Sauter et al., 2006). Models targeted at understanding the behavior of a single bubble ascending the seawater column utilizing observed methane concentration profiles (and other constituent boundary conditions, such as T, DO, salinity, etc) have been

* Corresponding author. Tel.: +81 11 706 2288; fax: +81 11 706 4865.
E-mail address: akitomo@ees.hokudai.ac.jp (A. Yamamoto).

developed (Leifer and Patro, 2002; Zheng and Yapa, 2002; McGinnis et al., 2006). According to model results for the case of the Black Sea, only a methane bubble released from the sea-floor at a depth of 100 m or less can reach the atmosphere, but this is minor (McGinnis et al., 2006). A huge methane flux would allow the released methane bubbles to rise 2000 m to the surface, and emit methane to the atmosphere due to the effect of forming a buoyant plume (Kourtidis et al., 2006).

Massive methane release due to decomposition of methane hydrate in sea-floor sediments might have caused rapid global warming in the past (Dickens et al., 1995; Kennett et al., 2002; Hinrichs et al., 2003). The Paleocene/Eocene thermal maximum (PETM), which took place about 55 million years ago, has been identified with negative excursions of the carbon isotopic composition of seawater, $\delta^{13}C$, up to 2.5–5‰, and global warming of 1–8 °C which occurred within the period of a few thousand years (Kennett and Stott, 1991; Zachos et al., 2003). According to hypotheses, the carbon isotope excursion and global warming during PETM might be linked to a methane release of ~2000 GtC derived from the destabilization of methane hydrate (Dickens et al., 1995; Katz et al., 1999; Bains et al., 1999) and/or the generation of metamorphic methane from sill intrusion into carbon-rich sedimentary rock in the Northeast Atlantic (Svensen et al., 2004; Storey et al., 2007). At present, a methane release of this magnitude due to decomposition of methane hydrate would pose the risk of accelerating the present ongoing global warming as is thought to have occurred during past climate change (Archer and Buffett, 2005; IPCC, 2007).

Except in the case of a huge methane flux, methane bubbles would not reach the atmosphere in a small seep as observed today. However, in the case of methane release from a large area (such as ~10^5 km^2 suggested by Svensen et al. (2004)), even if the methane flux is not large enough for direct atmospheric release, the regional methane concentration in the seawater would increase sufficiently to allow methane bubbles to reach the atmosphere. This study investigated whether the massive methane released from a sufficiently large sea-floor area could reach the atmosphere or not, focusing on methane saturation in the water column required for a methane bubble to reach the atmosphere. We developed a one-dimensional numerical model integrated over time for predicting the vertical distribution of methane bubbles and methane concentrations in the water column under the condition of continuous methane input from the sea-floor. We calculated the methane saturation in the water column and methane input from the sea-floor required for the methane bubble reaching the atmosphere, using this model, and investigated possible candidates for the controlling factor to determine the methane release ratio, such as initial bubble radius, seawater temperature, water depth, and methane oxidation. We compared the area density of the required methane input to that of methane amount in the sediment in the form of methane hydrate and free gas, and that of thermogenic methane generated by intrusion into carbon-rich sediments. We will discuss the possibility of global warming due to methane release caused by decomposition of sea-floor methane hydrate.

2. Model

In massive methane release events occurring in a large area, the horizontal diffusion throughout the release area, except at the border, could homogenize the gas concentration in the seawater among thousands of release points with in the area, but could not work dilution due to water exchange with the water outside the area. As a simplification, we assumed that the released methane bubbles are uniformly generated from an infinite area. Under this assumption, we can discuss the possibility of methane release to the atmosphere by comparing area density of the methane amount in the sediment with that input from sea-floor required for methane bubbles to reach the atmosphere. Hence, the advection and diffusion processes are not

included in our model. The methane concentration in the seawater obtained in this study should be interpreted as an upper estimate, and the required methane input for methane bubbles reaching the atmosphere is a lower estimate. The influence of these processes on the results is discussed in the Appendix.

Our one-dimensional numerical model combines the bubble and water column components in order to simulate the interaction between the bubbles and the gas concentrations in the seawater under the condition of continuous methane input from the sea-floor. We calculated the methane saturation in the water column and methane input from the sea-floor necessary for the methane bubble to reach the atmosphere, using this model. Our model cannot be applied to a huge methane flux, because the effect of forming plume and rising water parcel with bubbles, as suggested in Kourtidis et al. (2006), is not considered in our model's bubble component. In extraordinary methane flux, the required methane input necessary to release methane to the atmosphere would be much smaller than that calculated by our model.

2.1. Bubble component

There are extant models for a bubble rising in fluid which can be applied to a methane bubble rising in seawater (Clift et al., 1978; Leifer and Patro, 2002; Zheng and Yapa, 2002; McGinnis et al., 2006). We developed a bubble component calculating the developing process of an individual rising methane bubble with stripping and redissolution of oxygen and nitrogen based on McGinnis et al. (2006) and Zheng and Yapa (2002). We solved the equation of motion which considers the ascent of a bubble, gas transfer due to diffusion, and the equation of state for methane as a non-ideal gas. In these basic equations, we used the bubble ascent velocity from McGinnis et al. (2006), the gas transfer coefficient from Zheng and Yapa (2002), and the Peng–Robinson equation of state which includes pressure effects at great depths (Peng and Robinson, 1976). We also used a modified Henry's law (King, 1969). Henry's coefficients for methane is taken from Rettich et al. (1981) and for nitrogen and oxygen from Wüest et al. (1992).

Within the hydrate stability zone (HSZ), bubble dissolution is much slower than that above the HSZ (Merewether et al., 1985; Rehder et al., 2002; Greinert et al., 2006), since the formation of a hydrate rim around the bubble has already been proposed and observed (Brewer et al., 2002). In this area, we changed the exponent on the diffusion equations form 1/2 to 2/3 based on McGinnis et al. (2006). Because a bubble bigger than 1 cm is unlikely to exist and would likely break apart (McGinnis et al., 2006), we assumed that such a bubble would break apart into two bubbles.

We traced individual bubbles rising through the water column from the sea-floor: some bubbles can reach the surface but some are reduced in transit to $r = 0$ cm. Since the observed mole fraction of methane in a bubble at the sea-floor is more than 90% (Clark et al., 2000), the initial mole fraction of methane bubble was assumed, for simplicity, to be 100%.

2.2. Water column component

The water column is assumed that the depth is 5–2000 m, a grid size is 1 m^2 (area) × 5 m (height), and the seawater was assumed to be at rest. The concentrations of methane, oxygen and nitrogen in the water column are calculated in the water column component. The rate of change of the gas amount in the water column is given by

$$\frac{\partial C_i}{\partial t} = \frac{S_i}{V} - \gamma C_i - e_i C_i |_{\text{surface}}, \tag{1}$$

where $C_i(\text{mol/m}^3)$ is the gas concentration for gas species. $S_i(\text{mol/s})$ is the flux of dissolved gas from bubble to the water column calculated from the bubble component. It is assumed that the dissolved gas from

the bubble is immediately diluted with seawater of 5 m^3 (1 cell, V). The factor γ is the methane oxidation coefficient which is assumed to be 1.5 yr^{-1} for that portion of the water column deeper than the depth of 370 m and 10 yr^{-1} for that portion of the water column shallower than the depth of 370 m (Valentine et al., 2001), and e_i(yr^{-1}) is the gas exchange coefficient between the atmosphere and the ocean, which is based on Wanninkhof (1992), assuming a wind speed of 5 m/s. The initial concentrations of methane, oxygen, and nitrogen in the water column are zero, 0.3 mol/m^3, and 0.6 mol/m^3 for all depths, respectively. The seawater temperature and salinity were assumed to be global average values adopted from World Ocean Atlas 2001 (Conkright et al., 2002). The HSZ boundary is at the depth of 560 m based on a phase diagram for methane–seawater mixture (Tishchenko et al., 2005) and seawater temperature profile (Fig. 1).

We calculated the time evolution of a methane bubble released from the sea-floor in the bubble component, under the condition of methane concentration in the water column calculated in the previous time step. Using the vertical distribution of dissolved flux from this time-dependent evolution of the methane bubble in this time step, we calculated the temporal evolution of the methane concentration in the water column in the water-column component (Eq. (1)). Combining the two components, we can simulate the trend for successively released bubbles to dissolve more slowly and rise further before their entire dissolution than previously released bubbles, since the methane dissolved from prior bubbles increases the methane concentration in the water column. These processes are repeated until the methane concentration in the water column becomes sufficient for the bubble to reach the sea surface and enter the atmosphere.

We conducted the control experiment under the following conditions: a bubble radius of 0.3 cm which is consistent with observations (Egrov et al., 2003; Greinert et al., 2006; Sauter et al., 2006), sea-floor depth of 1000 m, the HSZ deeper than 560 m, and a methane flux of 2.5×10^{-2} mol/s·m^2 (equivalent to forty bubbles with a radius of 0.3 cm released per second into the water column from 1 m^2 of the sea-floor) which is the roughly the same order of magnitude to one order of magnitude more than the flux observed in a methane seep recently under investigation (Heeschen et al., 2003; Sauter et al., 2006). We conducted the case studies with different values by chang-ing four parameters: bubble radius, seawater temperature, water depth, and methane oxidation.

3. Results

3.1. Control experiment

We conducted the control experiment based on an integration period of 50 days (Figs. 2–4). The flux of 2.5×10^{-2} mol/s·m^2, is equivalent to forty bubbles with a radius of 0.3 cm released per second into the water column from 1 m^2 of the sea-floor. On the 1st day, the methane bubble rises up to a depth of about 550 m at which level it has completely dissolved into the surrounding seawater (Fig. 2). Methane concentration in the water column increases with time (Fig. 3a). The bubble released on the 25th day dissolves more slowly than that released on the 1st day, and rises to a depth of about 300 m before entirely dissolving. The bubble size does not change until 2200 s when the bubble enters in the HSZ, because reduction of bubble size due to dissolution is balanced by growth due to reduction of hydrostatic pressure with the bubble's ascent. The bubble rapidly dissolves at depths shallower than 560 m where there is no longer a hydrate rim. On the 50th day, the water column is almost saturated with methane (Fig. 3b). Thus, the bubble released on the 50th day dissolves only slightly, and can reach the sea surface. The bubble expands on its ascent by the effect of pressure reduction, and divides into two bubbles twice.

The methane concentration and degree of saturation in the water column increase from the deep ocean with time (Fig. 3a, b). A reversal of the methane concentration and degree of saturation with depth begins at the depth of 560 m, since the gas transfer coefficient in the HSZ is reduced to 20% rate of the non-rimmed bubble. When the methane concentration is close to saturation, this reversal becomes small because of the pressure dependence of the saturation concentration. The increase in the saturation fraction above the HSZ from 0 to 90% is very fast, because dissolution rate and saturation concentration above the HSZ are faster and smaller than those in the HSZ, respectively.

The bubble begins to reach the sea surface on the 33rd day (Fig. 4) when the methane saturation in the water column approaches about 80% or more in the HSZ and 100% above the HSZ. Since the bubble begins to reach the sea surface after the water column is almost saturated with methane, a release ratio, the ratio of methane released into the atmosphere to methane input from the sea-floor, rapidly rises to 80% around 40th day. After the water column in the HSZ is close to saturation, the release ratio slowly approaches 100%. Assuming that all the methane injected into the water column dissolves into the sea-water without being released into the atmosphere, we can easily estimate how many days are required for the whole water column to become saturated with methane from the amount of methane required for saturation divided by methane input flux (hereafter we call this a "simple estimation"). It is, estimated to take 38 days for a water column of 1000 m to become saturated with methane, at the methane flux of 2.5×10^{-2} mol/s·m^2. The 33rd day, at which time the methane bubble begins to reach the sea surface in the simulation, corresponds to the vertically integrated methane amount of 87% of the saturated methane quantity derived by the simple estimation above.

The oxygen concentration decreases in the deep water due to methane oxidation and bubble stripping before the oxygen concentration in the bubble equilibrates with that in seawater (Fig. 3c). The oxygen stripped by the bubble redissolves in the shallow water after the equilibrium. Under the condition of the sufficient low concentration of oxygen in the water column, the oxygen in the water column only dissolves into the bubble without equilibrium, and the oxygen in the bubble is released to the atmosphere without redissolving. The oxygen removal rates due to bubble stripping are much greater than those by oxidation. The concentration of nitrogen in the water column also changes due to bubble stripping and redissolution (Fig. 3d).
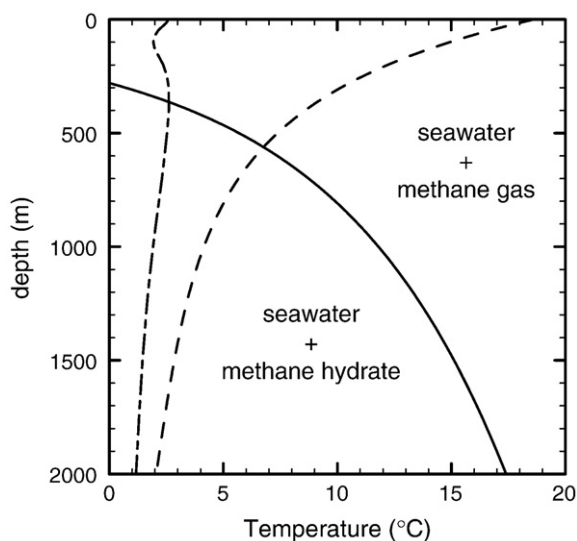
Fig. 1. Seawater temperature: globally-averaged (dashed line) and averaged in the high latitudes (>50°) (dashed-dotted line), used in this model; and phase diagram (solid lines) for methane–water mixture as a function of pressure and seawater temperature. Seawater temperature is based on World Ocean Atlas 2001 (Conkright et al., 2002). The phase diagram is based on Tishchenko et al. (2005).
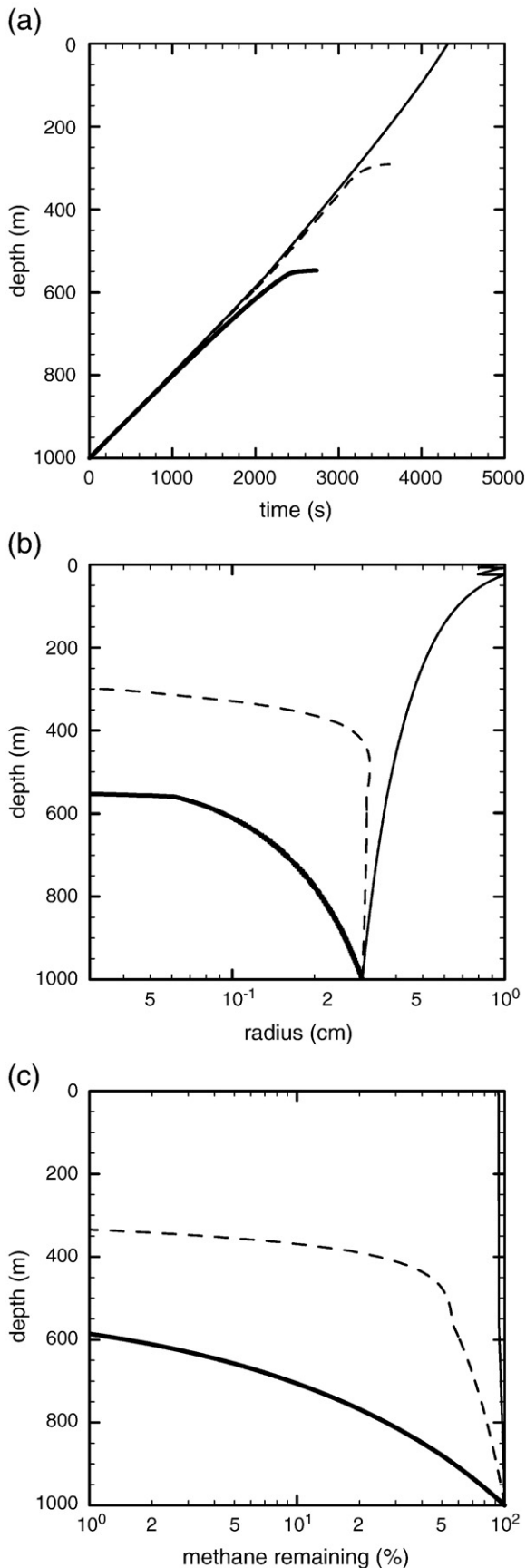
Fig. 2. The time evolution of (a) depth, and the evolution of (b) radius and (c) molar content of a bubble released from the sea-floor at 1000 m depth with depth. Solid, dashed and thin lines represent the bubble released on the 1st day, 25th day, and 50th day, respectively, from the beginning of methane release.

The amount of nitrogen dissolved into the bubble is greater than that of oxygen. That is, the decrease rate of nitrogen in the deep water is slower than that of oxygen, and the nitrogen concentration in the shallow water is higher than that of oxygen.

3.2. Sensitivity studies

We conducted sensitivity studies by changing values of the four parameters with the same methane flux of 2.5×10^{-2} mol/s·m^2 (Fig. 5), in order to investigate which parameters have a significant influence on the methane amount required for the methane bubble reaching the atmosphere.

In the case of an initial bubble radius of 0.6 cm, the bubble will reach the sea surface on the 19th day when the water column attains 50% methane saturation (Fig. 5a). This bubble that has eight times greater content and rises higher than the bubble in the control experiment reaches the atmosphere, even if the methane saturation in the water column is lower than that in the control experiment. Thus the first time a methane bubble reaches the atmosphere is much earlier than that in the control experiment. Also, the time the release ratio reaches 80% is delayed to around the 50th day, which is 10 days later than that in the control experiment. The calculated release ratio rises more slowly than that in the control experiment, because the methane tends to escape to the atmosphere without accumulating in the water column. The large-sized bubble is advantageous to decrease the time when the first methane bubble reaches the atmosphere, but does not always favor a large methane release ratio.

When seawater temperature is increased by 5 °C, the bubble will reach the sea surface on the 31st day when the water column becomes 91% saturated in methane (Fig. 5b). The amount of methane required for the water column to become saturated is smaller due to the higher temperature, compared with the control experiment. The simple estimation results in a 34th day saturation of the water column, which is 4 days faster than that in the control experiment. However, the first time when the bubble reaches the atmosphere is only 2 days earlier. This is because the warmer seawater reduces the HSZ thickness to 190 m (the HSZ boundary is at a depth of 810 m), and the bubble does not rise higher than that in the control experiment. The reduction of the HSZ cancels out the reduction of the amount of methane necessary for saturation by the temperature increase. Therefore, the time first methane bubble reaches the atmosphere changes minimally as a result of increasing the seawater temperature by 5 °C. Since the calculated methane saturation in the water column when the bubble reaches the sea surface is higher than that in the control experiment, the methane release ratio rises more rapidly and reaches 80% on the 34th day.

At a water depth of 1500 m, the amount of saturated methane in the water column is about double that in the control experiment, and it takes 78th days for the water column to become saturated, as determined by the simple estimation method. The bubble reaches the sea surface on the 70th day when the methane saturation in the water column becomes 90% (Fig. 5c), which is almost the same saturation observed in the control experiment. Since the calculated bubble rising with almost the same velocity as the experimental bubble passes through 1500 m from the sea-floor to the sea surface instead of 1000 m as in the control experiment, the total methane flux dissolved from the bubble needs to be about 1.5 times as great as that in the control case. However, the same size of bubble at a depth of 1500 m contains about a 1.5 times greater the amount of methane as that contained at the 1000 m depth. The bubble, therefore, reaches the atmosphere under roughly the same methane saturation conditions (i.e., 90% vs. 87%). The release ratio rises rapidly to 80% by the 85th day, but thereafter slowly approaches 100%.

The methane oxidation rate is an uncertain parameter. We conducted parameter studies with double the oxidation rate and without
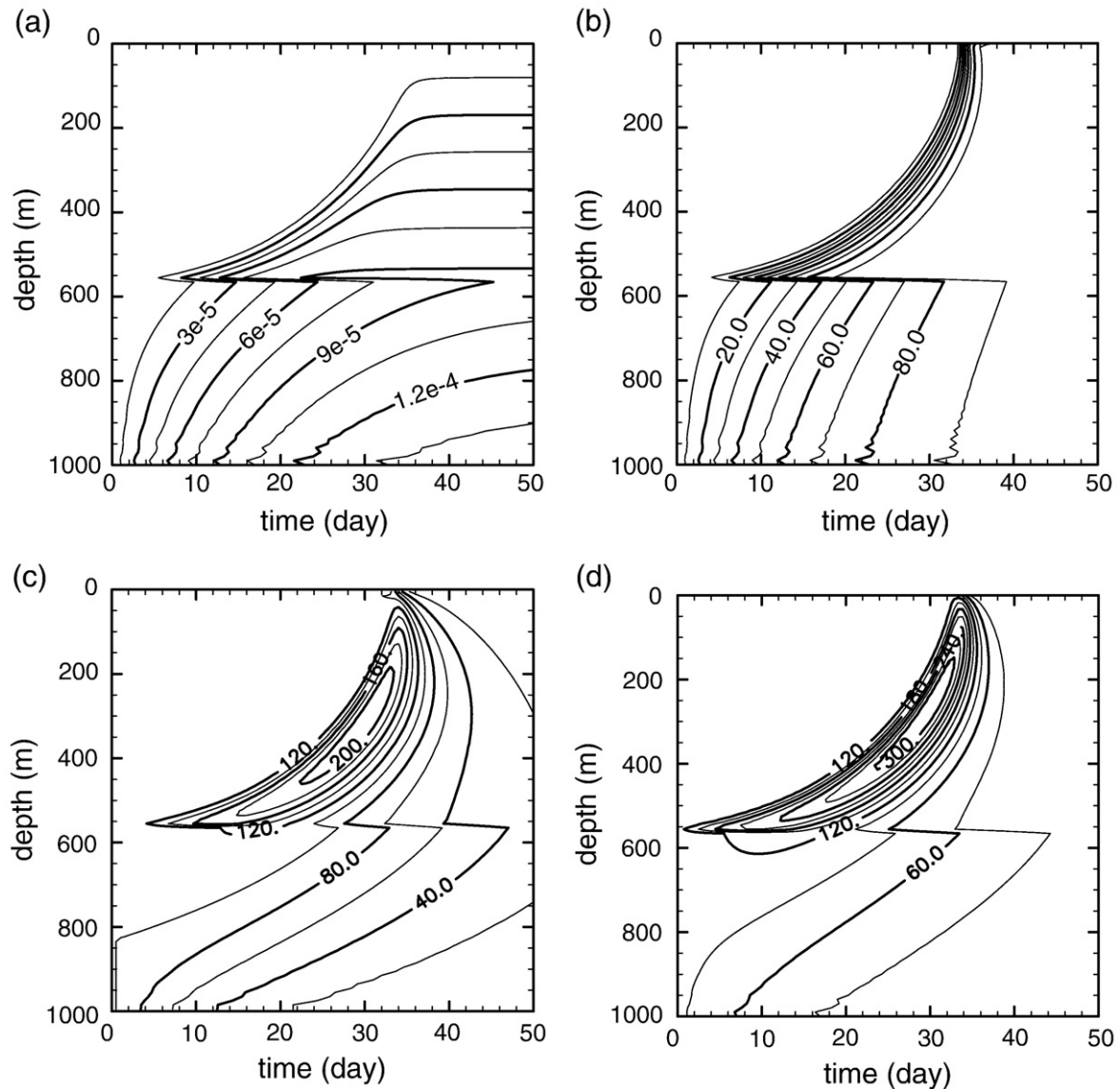
Fig. 3. Time evolution of (a) methane concentration (C.I = 1.5×10^{-5} mol/cm³) and (b) saturation fraction in the seawater (C.I = 10.0%). The time evolution of the percentage of (c) dissolved oxygen (C.I = 20.0%) and (d) nitrogen (C.I = 30.0%) concentration to the initial concentration in the water column.

oxidation. In these cases, the methane saturation in the water column required for the methane bubble to reach the atmosphere is not significantly affected, because methane reduction due to methane oxidation insignificantly changes the methane concentration in water column. The amount of dissolved oxygen is very small compared with that of dissolved methane in saturated seawater.

We also conducted the case studies with different values of methane flux input. The results are almost the same except for time-dependent changes in depths of the ascending bubble, increase in methane concentration in the water column, and so on (i.e., if methane flux is 10 or 1/10 times that in the control case, the timescale is 10 times faster or slower, respectively). This is because the timescales of all the behaviors are regulated by methane flux.

Comparing the sensitivity studies with the control experiment, the bubble radius and water depth essentially affect the amount of methane required for the methane bubble reaching the atmosphere. The simple estimation is a good approximation of the time at which most of the methane has been released into the atmosphere (i.e., at a methane release ratio of >80%) rather than the time when the first methane bubble reaches the atmosphere.

4. Discussion

We compare the area density of minimum methane input from the sea-floor necessary for methane to reach the atmosphere with that of the amount of methane contained in sediments in the compound methane hydrate. The volume of methane stored in the sediments in the form of hydrate, V, can be calculated from

$$V = A \times z \times \phi \times H \times G, \qquad (2)$$

where A is unit area of hydrate-bearing sediments ($= 1$ m²), z(m) is the thickness of the gas hydrate occurrence zone, ϕ is porosity, H is gas hydrate volume fraction in pore space, and G (m³/m³) is gas hydrate yield. The value of ϕ and G are obtained from Kvenvolden and Claypool (1988). HSZ is calculated from seawater temperature, the pressure–temperature relation for the methane hydrate stability condition, and the assumption of a geothermal gradient of 0.03 °C/m. We assume that the thickness of the gas hydrate occurrence zone is z 100 m thinner than that of the HSZ in sediments, based on the numerical model for the formation of methane hydrate in sediment
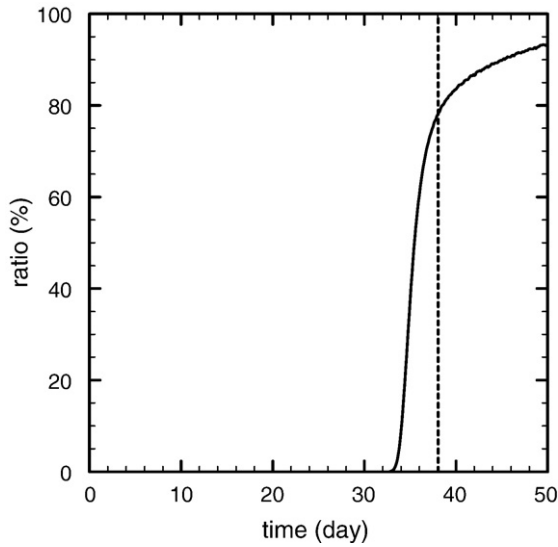
Fig. 4. Time evolution of the ratio of the methane reaching the atmosphere to that released from the sea-floor. The dotted line indicates the day when the water column becomes saturated with the methane, under the condition that all methane injected into the water column is dissolved into the seawater.

(Davie and Buffett, 2003). In the case of globally-averaged seawater temperature, methane hydrate exists in the sea-floor deeper than 600 m where the HSZ in sediments is thicker than 100 m. For example, the calculated is z 210 m at a sea-floor depth of 1000 m and 495 m at a sea-floor depth of 2000 m. We treat H to be a parameter because of its uncertainty. Under the condition of H at 10%, the calculated area density of methane amounts in sediments are 7.3×10^4 mol/m^2 at the sea-floor depth of 1000 m and 17.7×10^4 mol/m^2 at a sea-floor depth of 2000 m (Fig. 6).

Here, we estimate the area density of minimal amounts of methane inputs with sea-floor depth. The area density of minimal amounts of methane inputs for the initial bubble radii of 0.3 cm and 0.6 cm (which are often observed) corresponds to the amounts of 85–90% and 45–50% methane saturation in the water column, respectively (Fig. 6). To compare the minimum amount with methane amount in the sediment, we convert the former amount into "equivalent H" using Eq. (2). The equivalent H are estimated to be 9.5% (5%) and 14% (8.5%) at the sea-floor depths of 1000 m and 2000 m for an initial bubble radius of 0.3 cm (0.6 cm), respectively (Fig. 7a). Both the minimum amount of methane input and the methane hydrate amount in the sediment increase with depth (Fig. 6). The smallest value of the equivalent H is 5% at a sea-floor depth of 1000–1200 m, because the minimum amount of methane input and that of methane in the sediment have different depth dependencies. The depth dependency of the minimum amount of methane input in deep sea-floor is larger than in the shallow sea-floor, as the deeper seawater has the higher saturated methane concentration due to its higher pressure. On the other hand, the dependency of the amount of methane hydrate in the deep sea-floor is smaller than that in the shallow sea-floor (see Fig. 1). Therefore, the methane hydrate amount in the sediment which exceeds the minimum amount of methane input would not be found either in the deeper or shallower sea-floors. Recent estimates by direct measurement of methane concentration in sediments on Blake Ridge (Dickens et al., 1997) and Hydrate Ridge (Milkov et al., 2003) and by model for Blake Ridge and Cascadia Margin (Davie and Buffett, 2003) indicated that H is ~2%, and high volume fractions of methane hydrate are confined to localized faults (Davie and Buffett, 2003; Milkov et al., 2003). It is therefore implied that methane input from typical methane hydrate quantities in the sediment could supply the minimum amount of methane input only if H is unusually high or there are localized faults.
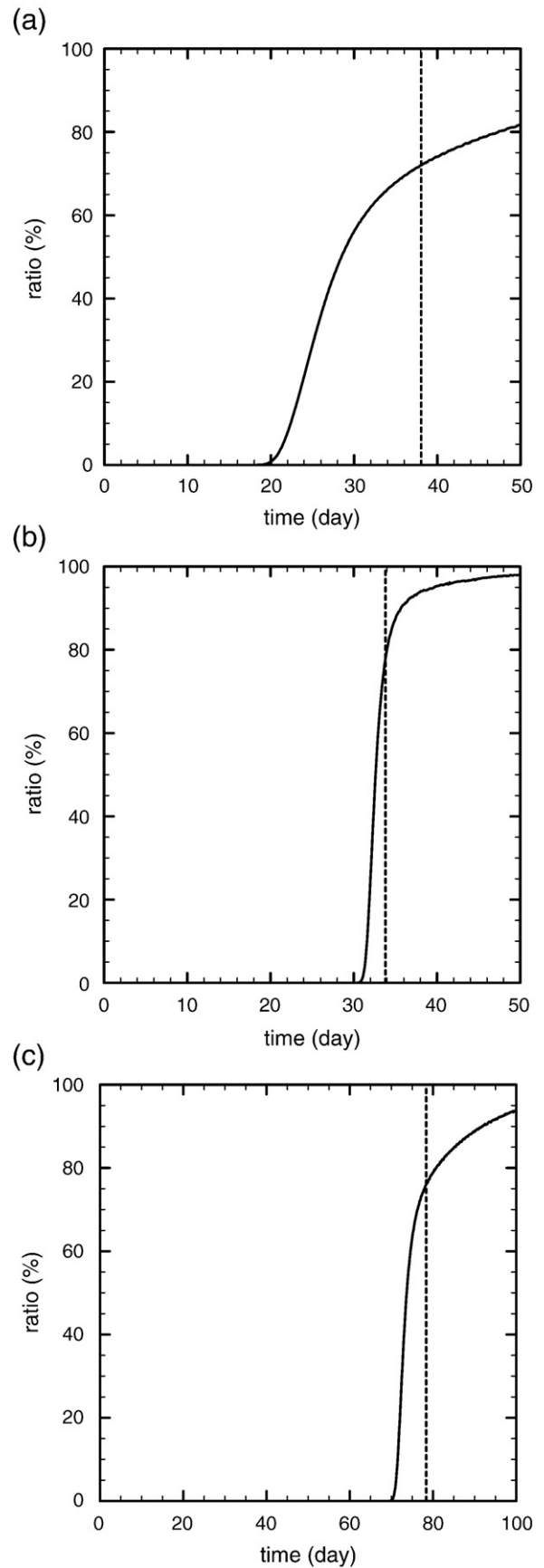
Fig. 5. Ratio of the methane reaching the atmosphere to the methane released from the sea-floor, under these initial conditions: (a) an initial bubble radius is 0.6 cm, (b) seawater temperature is 5 °C higher than that in the control experiments, and (c) the depth of sea-floor is 1500 m.
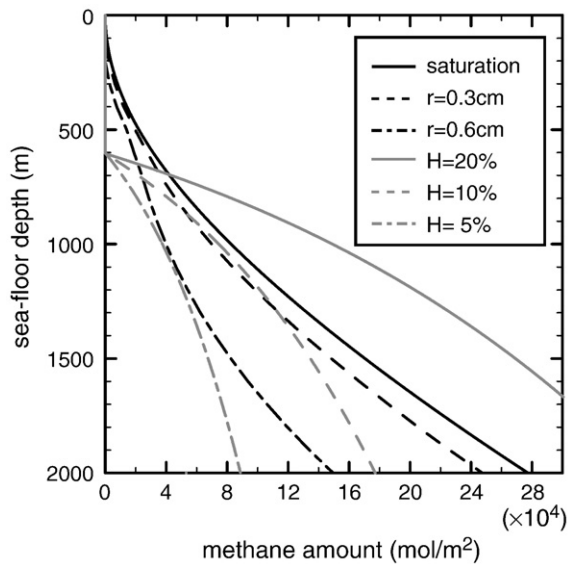
Fig. 6. The area density of minimum amount of methane input from the sea-floor required for the methane to reach the atmosphere (black line) and that of the amount of methane in the sediment as methane hydrate (gray line). Seawater temperature is assumed to be the global average. Black dashed and dashed-dotted lines represent initial bubble radii of 0.3 cm and 0.6 cm, respectively. For reference, the methane amount required for saturation in the water column is shown as black solid line. Gray solid, dotted, and dash-dotted lines represent a hydrate fraction H of 20%, 10%, and 3%, respectively.

Under the 5 °C warmer condition, the amount of methane in sea-floor sediments decreases due to reduction of the thickness of gas hydrate. The minimum amount of methane input changes minimally under the condition of seawater warming: a little decrease in initial bubble radius of 0.3 cm and a little increase in that of 0.6 cm, respectively. The difference is caused by the balance between a decrease in the methane amount for saturation in the water column and an expansion of the HSZ in the water column. Since the change in the minimum amount of methane input is smaller than the decrease in the methane amount in the sediment, the estimated equivalent H is larger than that in the case described earlier (Fig. 7b). The smallest equivalent H for initial bubble radii of 0.3 and 0.6 cm are 21% and 14%, respectively, at a sea-floor depth of 1600–1800 m. If the seawater becomes warmer, it is more difficult for the methane bubble released from the sea-floor to reach the atmosphere.

In high latitude regions (50° or more), the temperature of seawater shallower than 1000 m in depth is much lower than the global average (Fig. 1), and a large amount of methane hydrate has been found as a result of an increase in the thickness of the gas hydrate occurrence zone due to the low seawater temperature. Methane hydrate exists in sediments at sea-floor depths greater than 350 m, and the calculated thickness of the gas hydrate occurrence zone at 1000 m sea-floor is 1.4 times larger than that under the condition of globally-averaged seawater temperature. The minimum amount of methane input, however, changes slightly for different seawater temperatures. The smallest equivalent H values for the initial bubble radii of 0.3 and 0.6 cm are 5% and 2.3%, respectively, at a sea-floor depth of 600–900 m (Fig. 7c).

Methane as free gas exists under the methane hydrate layer. The methane amount of free gas was estimated to be less than two-thirds that of methane hydrate (Hornbach et al., 2004; Buffett and Archer,

2004). Even if we consider the methane amount of free gas plus methane hydrate, the amount of methane in the sea-floor sediments is much smaller than that which is required for reaching the atmosphere
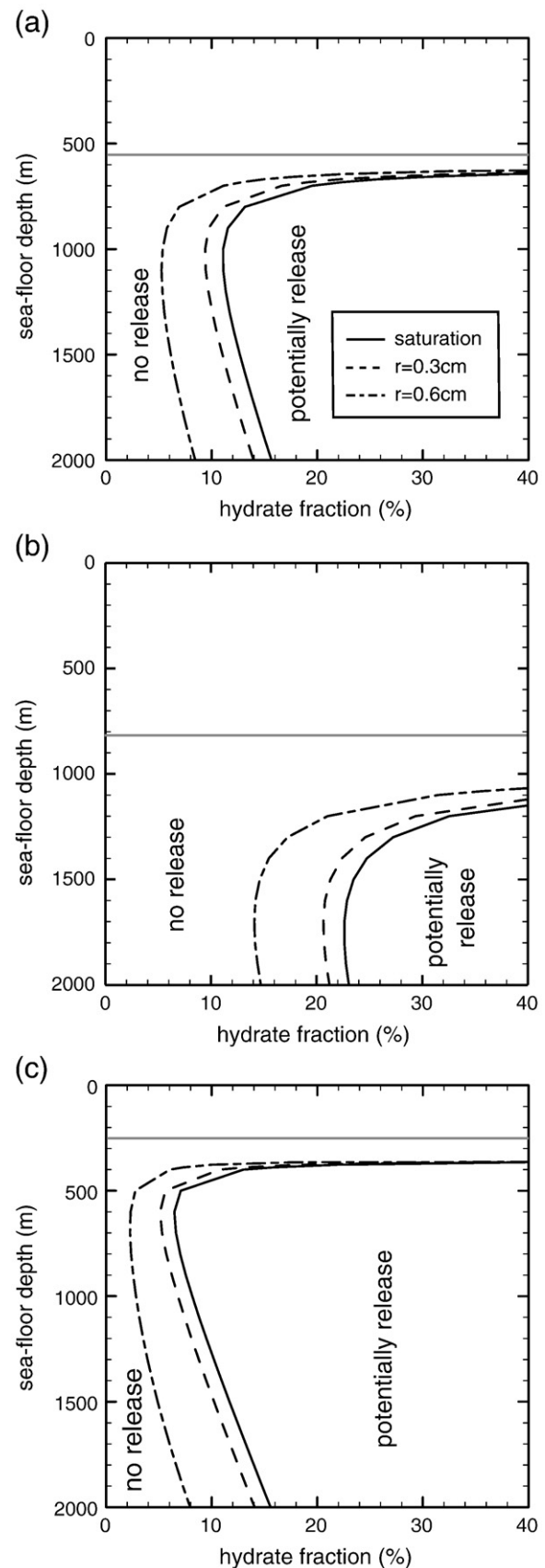
Fig. 7. The calculated equivalent H for the methane hydrate amount in the sea-floor sediment equivalent to the minimum amount of methane input (black line). The assumed seawater temperature is (a) the global average, (b) 5 °C higher than the global average, and (c) averaged for the high latitudes (>50°). Black dashed and dashed-dotted lines represent the cases for initial bubble radii of 0.3 cm and 0.6 cm, respectively. Gray horizontal line represents the boundary of HSZ.

under the conditions that the seawater temperature is the global average or 5 °C higher than the global average. Assuming special conditions, such as that in which the seawater temperature is averaged in the high latitudes (>50°), the sea-floor depth is 500–1000 m, and the bubble with an initial radius of 0.6 cm potentially reaches the sea surface, only a negligible portion of the total methane hydrate in the sediment (<1.0×10^{-3}%) reaches the sea surface.

We also compared the area density of required minimum methane input from the sea-floor with that of the amount of methane produced in the metamorphic aureoles in the Northeast Atlantic after sill emplacement (Svensen et al., 2004). Svensen et al. (2004) estimate 0.2 to 2.2×10^6 mol/m^2 of methane which is roughly the same order of magnitude to one order of magnitude larger than the required methane input calculated by our model. It is suggested that the released thermogenic methane would result in methane-saturated seawater and that some methane would reach the atmosphere.

5. Summary and concluding remarks

We developed a one-dimensional numerical model in order to calculate both the ratio of methane flux reaching the atmosphere to that released from the sea-floor and methane saturation in the water column. The model results suggest that a methane bubble with a typical radius of 0.3–0.6 cm reaches the atmosphere when the methane saturation fraction in the water column is 90–45%. However, a release ratio reaches >80% after the water column reaches 90% saturation.

We compared the area density of minimum amount of methane input from the sea-floor required for a methane bubble to reach the atmosphere with that of the typical amount of methane in the sediments. The amount of methane in the sediments is smaller than the minimum amount of methane input needed to enter the atmosphere, in most cases. It is, therefore, difficult for the massive methane bubble release from the sea-floor to reach the atmosphere directly, except for special cases such as localized faults with a >10% hydrate fraction or a huge methane flux caused by submarine slides. For the case of warmer conditions, the minimum amount of methane input changes slightly while the methane amount in the sediment decreases. It is more difficult for the methane bubble released from the sea-floor to reach the atmosphere. The horizontal advection and diffusion processes would require greater input of methane in order to cause methane release into the atmosphere, i.e., we would need a greater amount of methane than the minimum methane input estimated by our model, shown in Appendix.

Applying our results to PETM, it is suggested that a methane bubble derived directly from the typical hydrate layer could not have contributed substantially to global warming. On the other hand, the methane derived from organic-rich sediments intruded by magma (Svensen et al., 2004) could be emitted to the atmosphere. The collapse of methane hydrate would potentially cause a global-scal anoxic condition in the seawater. The methane of 2000 GtC dissolved into the world ocean consumes 3.3×10^{17} mol of dissolved oxygen, which is about the same amount of dissolved oxygen as is in the ocean at the present. The dissolved methane from the methane bubble rapidly consumes in situ and surrounding dissolved oxygen owing to advection and diffusion on the time scale of hundreds of years. Advection and diffusion would determine distribution of the anoxic condition by influencing oxygen supply from the sea surface. In other words, these mixing phenomena would also determine the distribution of dissolved methane without oxidation that would reach the atmosphere. We need General Circulation Models (GCMs) to estimate the expansion of anoxic conditions in the ocean and the amount of methane released into the atmosphere.

As regards global warming due to human activities, Archer and Buffett (2005) suggested ~2000 GtC release of methane from sea-floor gas hydrate over 1 to 100 k yr, which is a similar methane magnitude of anthropogenic carbon release (IPCC, 2007). Our results indicate the methane release from the typical hydrate layer could not cause an abrupt climate change, through the methane release to the atmosphere.

Appendix A. Effects of horizontal advection and diffusion

We discuss the effects of horizontal advection and diffusion on the methane concentration in the water column. We treated the water column in our model as a horizontal box model. The advection and diffusion into and out of the water column were calculated as exchanges between the seawater in the water column and methane-free water surrounding the water column. This condition of water exchange gives us the most dilute condition. We conducted the supplemental experiments under the same conditions as in the control experiment except that we considered advection and diffusion processes with the constant flow speed of 1 cm/s and the horizontal diffusivity of 10^6 cm^2/s (e.g., Sundermeyer and Price, 1998), We integrated the model in 32 days, at which time the water column becomes 84% saturated in methane and the methane bubbles begins to reach the sea surface in the control experiment. We changed the width of the square of the water column from 10^{-1} to 10^3 km. In the scale of 10^{-1} to 1 km in width (typical seep observed), the methane saturation in the water column hardly increases, in that the dissolved methane from the bubble to the seawater is not accumulated but instantly diluted by the two processes. Our results excluding these two processes could not be applied to the observed methane seep. The methane concentration in the water column gradually increases 6.0 and 69.7% of methane saturation in column square widths of 10^1 and 10^2 km, respectively. In larger areas than 10^2 km, the methane saturation with advection and diffusion approaches the methane saturation without these processes due to long turnover time. Hence, in the case of methane release from a large area such as PETM, our assumption of uniform methane release from an infinite area is good for estimating methane concentration in the water column. As a future study, we need to calculate the advection and diffusion processes more strictly by use of a three-dimensional model, because the calculation of these processes is considerably idealized.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2009.05.026.

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