Methane escape from gas hydrate systems in marine environment, and methane-driven oceanic eruptions

Youxue Zhang

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, USA

[1]   Huge quantities of CH_4 are stored in marine sediment in the form of methane hydrate, bubbles, and dissolved CH_4 in pore water. Here I discuss the various pathways for methane to enter the ocean and atmosphere, including: (i) Methane hydrate dissolution or dissociation as it rises through seawater. The dissociation rate can be 2 to 3 orders of magnitude greater than the dissolution rate. (ii) The dissolution and expansion of a bubble with or without a hydrate shell as it rises through seawater. There is a critical radius (which depends on depth), above which a bubble would reach the surface or even become larger as it rises. I also propose and model the dynamics of a new type of terrestrial gas-driven eruptions: methane-driven oceanic eruptions. Such eruptions not only represent a yet unrecognized geohazard, but also provide a pathway for CH_4 to rapidly enter the atmosphere as a greenhouse gas.   INDEX TERMS: 3099 Marine Geology and Geophysics: General or miscellaneous; 4568 Oceanography: Physical: Turbulence, diffusion, and mixing processes; 8414 Volcanology: Eruption mechanisms; 8450 Volcanology: Planetary volcanism (5480); 9810 General or Miscellaneous: New fields (not classifiable under other headings). **Citation:** Zhang, Y., Methane escape from gas hydrate systems in marine environment, and methane-driven oceanic eruptions, *Geophys. Res. Lett.*, *30*(7), 1398, doi:10.1029/2002GL016658, 2003.

1.   Introduction

[2]   Conditions on many planetary bodies are suitable for gas hydrate stability [*Lunine and Stevenson*, 1985]. Enormous amounts of methane are stored as gas hydrate and free gas in the pore space of marine sediment [*Kvenvolden*, 1988; *Buffet*, 2000]. Mounting circumstantial evidence indicates that large quantities of this methane can escape the seafloor when certain external conditions change, such as a rise in bottom water temperature [*Dickens et al.*, 1995; *Kennett et al.*, 2000], a drop in sea level [*Paull et al.*, 1991], landslide, faulting, and/or bursting of methane gas [*Bugge et al.*, 1987; *Maslin et al.*, 1998; *Rothwell et al.*, 1998]. One outstanding and largely unexplored issue is the fate of methane. Once released at depth, methane hydrate and/or bubbles could potentially dissolve in water or rise to the ocean surface, perhaps even driving a limnic-type eruption [*Kling et al.*, 1987; *Zhang*, 1996, 1998a; *Clark et al.*, 2000; *Kennet et al.*, 2000; *Leifer et al.*, 2000]. In this report, I address the potential fate of methane escaping gas hydrate systems.

2.   Stability of Methane Phases in the Marine Environment

[3]   Methane can exist in the marine environment as gas hydrate, free gas or dissolved in water. To illustrate the stability of methane hydrate, methane gas, and dissolved methane in seawater, a phase diagram is constructed for the CH_4-seawater system along a T-P-depth profile similar to Blake Ridge (east of the Carolina coast), a site with a large reservoir of methane in the form of hydrate and gas [*Holbrook et al.*, 1996; *Dickens et al.*, 1997]. Figures 1a and 1b show the temperature and pressure profile. Figure 1c shows the phase diagram along the depth and is explained below. From the sea surface to a shallow depth in the water column ($\leq$537 m below sea level, mbsl), methane hydrate is not stable. If total CH_4 concentration is low, all CH_4 would dissolve in water; if total CH_4 concentration is greater than the solubility (which increases roughly linearly with depth to 0.127 wt% (0.081 mol/L) at 537 mbsl [*Duan et al.*, 1992]), then extra CH_4 would be in the gas phase (bubbles). From 537 mbsl to 3225 mbsl (450 m below seafloor, mbsf), methane hydrate is stable if CH_4 concentration in the system is high enough. The formation of methane hydrate limits the solubility of CH_4 in water [*Dickens and Quinby-Hunt*, 1994]. From 537 mbsl to the seafloor (2775 mbsl), temperature decreases slightly with increasing depth and the requisite pressure for hydrate formation decreases. Hence, hydrate becomes more stable with increasing pressure, leading to a slight decrease in the solubility of CH_4 from 0.127 wt% at 537 mbsl to 0.107 wt% at 2775 mbsl. From 2775 mbsl to 3225 mbsl (seafloor to 450 m blsf), temperature increases with depth, and hence the formation pressure of methane hydrate increases with depth. Therefore, methane hydrate stability decreases and CH_4 solubility in pore water increases with depth to 0.3 wt% at 3225 mbsl. Below this depth, methane hydrate is not stable due to high temperatures. Instead, oversaturation of CH_4 leads to the formation of gas bubbles in pore water. For other locations, temperature profiles and water depths can differ, leading to different phase diagrams. For example, if water depth is only 500 m and the temperature-depth profile is the same as the top 500 mbsl at the Blake Ridge, there would be no hydrate stability field.

3.   Methane Escape Mechanisms
3.1.   Rise of Hydrate

[4]   Density of hydrate is smaller than that of seawater. Whether released hydrate would rise depends on how much sediment is mixed in it. If mixing of sediment is insignificant, methane hydrate would rise buoyantly through the water column either individually or collectively with other hydrate
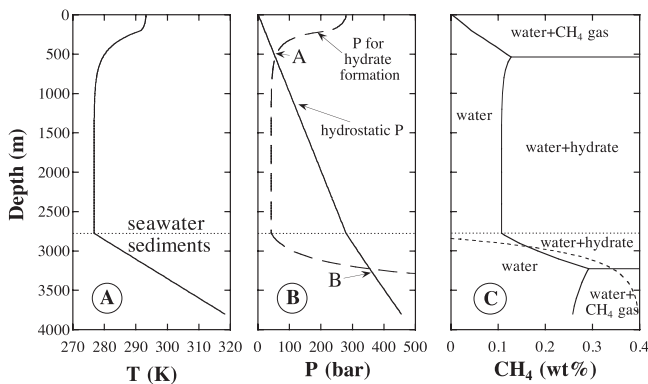
Figure 1. (a) Temperature as a function of depth in oceans (roughly for the case of Blake Ridge east of Carolina). The dashed horizontal line in (a), (b) and (c) marks the seafloor. (b) Variation of both the hydrostatic pressure (solid curve) and the hydrate-stability pressure (dashed curve, calculated from *Dickens and Quinby-Hunt* [1994]) with depth. (c) A calculated phase diagram for the CH$_4$-seawater system in terms of depth along which both T and P are varying as shown in (a) and (b) (instead of a phase diagram in terms of P at constant T, or in terms of T at constant P). Phase boundaries are shown as solid curves and lines. Note that the scale for CH$_4$ concentration only goes to 0.4 wt% CH$_4$. The solubility of CH$_4$ in seawater as a function of T and P is calculated from *Duan et al.* [1992]. When methane hydrate is more stable, the solubility is calculated based on equilibrium with methane hydrate [*Dickens and Quinby-Hunt*, 1994]. The long-dashed curve is a hypothetical profile of total CH$_4$ concentration in pore water due to decomposition of organic matters before any modification by mass transport or compaction. See *Dickens et al.* [1997] for actual total CH$_4$ concentration profile in pore water.

crystals. We have extended the model of *Kerr* [1995] to high Reynolds numbers to calculate the convective dissolution rate upon buoyant rising, and the model of *McLeod and Sparks* [1998] to calculate convective dissociation rate upon rising [*Zhang and Xu*, submitted]. In deep water, hydrate dissolves as it rises. At 4°C (for deep water), a typical calculated convective dissolution rate is 0.2 to 0.3 μm/s. A crystal with an initial radius of 5.2 mm would dissolve completely after a 2000−m rise. In shallow water, hydrate dissociates as it rises. At 20°C (for shallow water), a typical calculated convective *dissociation* rate is 0.1 mm/s, greater than the *dissolution* rate in deep water by 2 to 3 orders of magnitude. A crystal with an initial radius of 5 mm would completely dissociate after only a 3-m rise. Modeling using a more realistic temperature-depth profile shows that hydrate chunks larger than 100 mm radius would be able to survive dissociation through a 530-m surface layer and reach the ocean surface [*Zhang and Xu*, submitted].

3.2. Rise of a Bubble

[5] If methane bubbles are released slowly into shallow seawater where hydrate is not stable (e.g.,<537 mbsl, Figure 1c), bubbles rise through water individually or in streams [*Brewer et al.*, 1997; *Clark et al.*, 2000; *Leifer et al.*, 2000]. As a bubble rises, it dissolves in seawater (which is almost always CH$_4$-undersaturated), and expands as the pressure

decreases. The dissolution makes the bubble smaller. The expansion makes the bubble larger. Whether the size of the bubble would increase or decrease depends on the interplay between dissolution and expansion. *Zhang and Xu* [2001] developed a model for the convective dissolution rate of a spherical bubble as it rises buoyantly through seawater, but nonspherical bubbles (those with radius greater than 1.5 mm) can only be roughly treated. For a given depth, there is a critical bubble size, above which bubble size increases, and below which the bubble size decreases as it dissolves and rises. The critical radius for a bubble to survive 50-m rise is 0.9 mm. Bubble rise velocity is typically ≤0.3 m/s.

3.3. Rise of a Bubble With Hydrate Shell

[6] If a methane bubble is released into deep water where methane gas and water would react to form hydrate (≥537 mbsl, Figure 1c), a thin hydrate shell may form on the bubble. As the bubble with a thin hydrous shell rises, hydrate would dissolve. Furthermore, gas in the bubble would expand, cracking the hydrate shell. Nevertheless, any new contact between CH$_4$ in the bubble and seawater would lead to new hydrate formation. Hence there would be a delicate balance between dissolution of methane hydrate shell, and its reformation, leading to a steady-state CH$_4$ mass loss from the bubble. Since hydrate is more stable than CH$_4$ gas, the solubility of hydrate in seawater is smaller than that of a CH$_4$ bubble. Hence the formation of a hydrate shell slows down the dissolution. Calculation shows that if the initial bubble radius is 3 mm or greater, the bubble with hydrate shell would be able to survive from any depth to shallow water.

3.4. Methane-Driven Ocean Eruptions

[7] In the special case of a sudden release of a large amount of pore water that is oversaturated with methane (containing hydrate and bubbles), such as during a large landslide, a methane-driven ocean eruption may occur. This would be similar to CO$_2$-driven lake eruptions [*Kling et al.*, 1987; *Sigurdson et al.*, 1987; *Sigvaldason*, 1989; *Zhang*, 1996; *Halbawachs and Sabroux*, 2001]. Gas-driven water eruptions have also been hypothesized to resurface Europa [*Crawford and Stevenson*, 1988].

[8] If CH$_4$-bearing water is released to shallow seawater (e.g., <537 mbsl, Figure 1c), methane hydrate is unstable. With a high bubble number density (number of bubbles per unit volume of water), bubbles would rise collectively as a bubbly water plume because bubbly water has a lower overall density than the surrounding water. As the bubbly plume rises, the volume of the gas phase expands due to pressure reduction. Hence, the density of the bubbly water decreases further, leading to more rapid buoyant rise of the bubbly water plume (Figure 2). This strong positive feedback is similar to what happens in CO$_2$-driven lake eruptions [*Zhang*, 1996], although the smaller solubility of CH$_4$ in water means that the eruption velocity would be smaller under the same saturation pressure.

[9] If hydrate- and bubble-bearing pore water oversaturated in CH$_4$ is released to deep water (> 537 mbsl, Figures 1c and 2), methane hydrate is stable, and CH$_4$ gas bubbles may react rapidly with water to form hydrate shells. Although there is always relative motion between hydrate, bubbles and
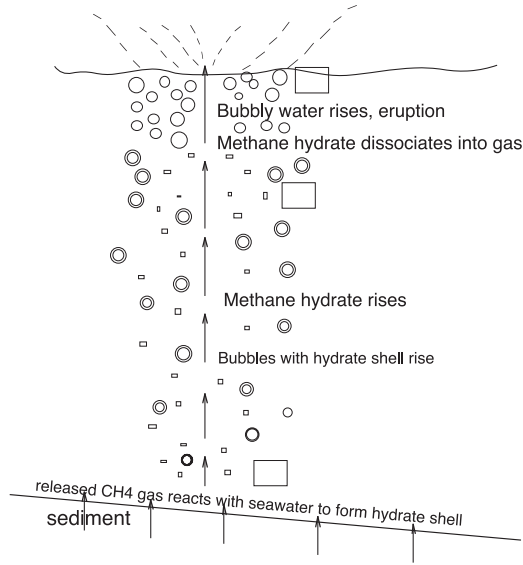
Figure 2. A schematic diagram for the dynamics of methane-driven eruptions. Rectangles represent methane hydrate crystals and aggregates; circles represent bubbles; double circles represent bubbles with methane hydrate shell.

water, the more interesting motion is the rapid rise (such as ≥ 1 m/s) of the whole parcel of water containing shelled bubbles and hydrate. Since the water parcel is supersaturated in CH_4, bubbles and hydrate would grow rather than dissolve. When the water parcel reaches shallow depths where hydrate is unstable, any hydrate shell on bubbles would dissociate rapidly, releasing the bubbles and producing a bubbly plume. Small hydrate crystals (<5 mm radius) reaching this shallow depth would also dissociate rapidly into methane bubbles and water, and become part of the bubbly plume. The ensuing dynamics of the bubbly water plume would follow that of release into shallow water, resulting in an eruption.

[10] The dynamics of methane-driven oceanic eruptions are modeled below, following the analyses for CO_2-driven lake eruptions [Zhang, 1996, 2000]. Since the initial gas phase can be significant at the depth of hydrate dissociation where the bubble plume forms, the mass fraction of the initial gas phase (δ_0) is explicitly included in the modeling. Assuming ideal gas law and equilibrium between the gas and liquid phases, and ignoring shallow water entrainment, the density of the gas-liquid mixture ρ can be expressed as follows [Zhang, 2000]:

$$\frac{\rho^l}{\rho} = 1 - \delta_0 + \delta_0 \frac{\rho^l RT}{P} + \lambda \frac{P_0}{P} - \lambda, \qquad (1)$$

where ρ^l is the liquid density, P is the pressure of the gas phase and is the same as the hydrostatic pressure, P_0 is the pressure at the initial depth at which hydrate dissociates and the bubble plume forms, T is the temperature, R is the gas constant for CH_4 (518.3 J kg^{-1} K^{-1}), and $\lambda = C^{liq}_{CH4}/C^{gas}_{CH4}$ is the Ostwald solubility coefficient and is assumed to be constant (λ depends weakly on T and P but the dependence is ignored for analytical solution below). Combining equation 1 and the

Bernoulli equation, and integrating, the following equation can be obtained:

$$\frac{1}{2}u^2 \approx \lambda \frac{P_0}{\rho^l}\left(\ln\frac{P_0}{P_{exit}} - 1 + \frac{P_{exit}}{P_0}\right)$$
$$+ \delta_0\left[RT\ln\frac{P_0}{P_{exit}} - \frac{P_0}{\rho^l}\left(1 - \frac{P_{exit}}{P_0}\right)\right], \qquad (2)$$

where P_{exit} is the exit pressure at the sea level, u is the velocity of the bubbly flow as it exits the ocean surface, and g is acceleration due to gravity.

[11] A more realistic model for the dynamics of CH_4-driven water eruptions would require consideration of entrainment and disequilibrium. Entrainment is especially important if the volume of release is small. Owing to the simplifying assumptions, equation 2 and the results below should be considered semi-quantitative. Figure 3 shows calculated maximum exit velocity as a function of the initial depth (at which methane hydrate dissociates to methane gas and water) for several δ_0 values and with $\lambda = 0.034$. Because the Ostwald solubility coefficient for CH_4 is smaller than that for CO_2 by a factor of about 30, CH_4-driven eruptions are much less violent under the same saturation conditions. For example, if initial water depth is 208 m and $\delta_0 = 0$, the maximum exit velocity would be only 18 m/s for CH_4-driven water eruptions, compared to 89 m/s calculated for CO_2-driven Lake Nyos eruption [Zhang, 1996]. However, the oceans are much deeper than lakes and mass and concentration of CH_4 in released pore water can be very large. For example, a 2000 km^3 landslide [Bugge et al., 1987; Maslin et al., 1998; Rothwell et al., 1998] might release pore water containing ≥ 1 Gt CH_4, 1000 times the volume of CO_2 released in the 1986 eruption of Lake Nyos [Kling et al., 1987]. The dissociation of thin hydrate shells and small hydrate crystals can also contribute initial CH_4 gas ($\delta_0 > 0$) in a large volume of water. Consequently, CH_4-driven oceanic eruptions have the potential to achieve greater exit velocities than CO_2-driven lake eruptions. Direct measurements show that pore waters in marine sediment may average
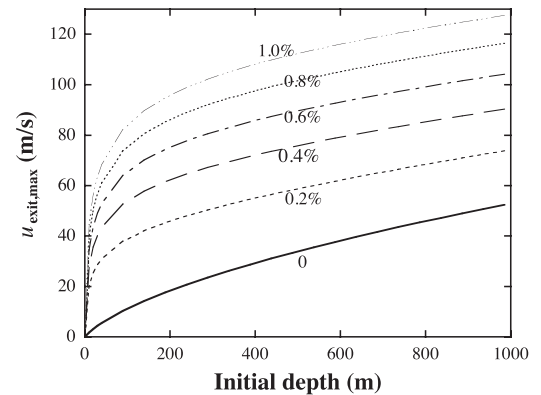

Figure 3. Calculated maximum exit velocity (using equation 2) as a function of initial depth. Fraction on each curve indicates the initial mass fraction of the gas phase (δ_0). The calculation is done for an exit pressure of 1 bar, T = 280 K, and $\lambda = 0.034$. The results are semi-quantitative because shallow water entrainment and disequilibrium between the gas phase and water are ignored.

1.1 wt% total CH_4 [*Dickens et al.*, 1997]. With such a concentration at 500 mbsl, the maximum exit velocity would be 110 m/s. With high exit velocity and large amounts of gas, oceanic eruptions could be very violent.

[12] In addition to the solubility difference between CO_2-driven and CH_4-driven water eruptions, another difference between them is that CH_4 gas is less dense than air whereas CO_2 gas is denser than air. Hence erupted CH_4 gas is expected to rise buoyantly into the atmosphere, instead of forming a ground-hugging "ambioructic" flow [*Zhang*, 1996], which was the killing agents in CO_2-driven eruptions. Therefore, CH_4-driven eruptions would only impact on those in the direct path of the rising column. Such eruptions would also provide a pathway for CH_4 in marine sediment to rapidly enter the atmosphere as a greenhouse gas.

[13] Methane-driven oceanic eruptions requires major slumps or other major disturbances. Such conditions are more easily met when there was wholesale warming of ocean bottom water. Hence, the thermal maximum at the Paleocene-Eocene boundary would be an optimum time for such eruptions, leading to rapid CH_4 transfer to the atmosphere as a climate driver. Furthermore, the magnitude of $\delta^{13}C$ excursion (about $-3‰$ [*Dickens et al.*, 1995; *Kennett et al.*, 2000]) is quantitatively consistent with CH_4 reaction with dissolved oxygen in deep seawater, as shown below. The concentration of dissolved O_2 is about 0.00022 M and that of HCO_3^- is 0.0023 M, with a $[O_2]/[HCO_3^-]$ concentration ratio of about 0.1. One mole of CH_4 reduces two moles of O_2. Hence complete depletion of deep water O_2 by oxidation of CH_4 would contribute 5% of total dissolved HCO_3^- in seawater. Assuming an average of $\delta^{13}C$ of $-60‰$ for CH_4, and $0‰$ for HCO_3^-, the resulting extent of $\delta^{13}C$ is $0.05 \times (-60‰)$, about $-3‰$. Locally the excursion can be greater or smaller because both dissolved O_2 content and the $\delta^{13}C$ value of CH_4 may vary. The depletion of dissolved O_2 in deep seawater would have major environmental consequences.

References

Brewer, P. G., F. M. Orr, G. Friederich, K. A. Kvenvolden, D. L. Orange, J. McFarlane, and W. Kirkwood, Deep-ocean field test of methane hydrate formation from a remotely operated vehicle, *Geology*, 25, 407–410, 1997.

Buffett, B. A., Clathrate hydrates, *Annu. Rev. Earth Planet. Sci.*, 28, 477–507, 2000.

Bugge, T., S. Befring, R. H. Belderson, T. Eidvin, E. Jansen, N. H. Kenyon, H. Holtedahl, and H. P. Sejrup, A giant three-stage submarine slide off Norway, *MGeo-Marine Lett.*, 7, 191–198, 1987.

Clark, J. F., L. Washburn, J. S. Hornafius, and B. P. Luyendyk, Dissolved hydrocarbon flux from natural marine seeps to the southern California Bight, *J. Geophys. Res.*, 105, 11,509–11,522, 2000.

Crawford, G. D., and D. J. Stevenson, Gas-driven water volcanism and the resurfacing of Europa, *Icarus*, 73, 66–79, 1988.

Dickens, G. R., J. R. O'Neil, D. K. Rea, and R. M. Owen, Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of Paleocene, *Paleoceanography*, 10, 965–971, 1995.

Dickens, G. R., C. K. Paull, P. Wallace, and T. O. L. S. Party, Direct measurement of in situ methane quantities in a large gas-hydrate reservoir, *Nature*, 385, 426–428, 1997.

Dickens, G. R., and M. S. Quinby-Hunt, Methane hydrate stability in seawater, *Geophys. Res. Lett.*, 21, 2115–2118, 1994.

Duan, Z., N. Moller, J. Greenberg, and J. H. Weare, The prediction of methane solubility in natural waters to high ionic strength from 0 to 250°C and from 0 to 1600 bar, *Geochim. Cosmochim. Acta*, 56, 1451–1460, 1992.

Halbwachs, M., and J. C. Sabroux, Removing CO_2 from Lake Nyos in Cameroon, *Science*, 292, 438, 2001.

Holbrook, W. S., H. Hoskins, W. T. Wood, R. A. Stephen, D. Lizarralde, and L. S. Party, Methane hydrate and free gas on the Blake Ridge from vertical seismic profiling, *Science*, 273, 1840–1843, 1996.

Kennett, J. P., K. G. Cannariato, I. L. Hendy, and R. J. Behl, Carbon isotopic evidence for methane hydrate instability during Quaternary interstadials, *Science*, 288, 128–133, 2000.

Kerr, R. C., Convective crystal dissolution, *Contrib. Mineral. Petrol.*, 121, 237–246, 1995.

Kling, G. W., M. A. Clark, H. R. Compton, J. D. Devine, W. C. Evans, A. M. Humphrey, E. J. Koenigsberg, J. P. Lockwood, M. L. Tuttle, and G. N. Wagner, The 1986 Lake Nyos gas disaster in Cameroon, West Africa, *Science*, 236, 169–175, 1987.

Kvenvolden, K. A., Methane hydrate - A major reservoir of carbon in the shallow geosphere?, *Chem. Geol.*, 71, 41–51, 1988.

Leifer, I., J. F. Clark, and R. F. Chen, Modifications of the local environment by natural marine hydrocarbon seeps, *Geophys. Res. Lett.*, 27, 3711–3714, 2000.

Lunine, J. I., and D. J. Stevenson, Thermodynamics of clathrate hydrate at low and high pressure with application to the outer solar system, *Astrophys. J. Suppl. Ser.*, 58, 493–531, 1985.

Maslin, M., N. Mikkelsen, C. Vilela, and B. Haq, Sea-level and gas-hydrate-controlled catastrophic sediment failures of the Amazon Fan, *Geology*, 26, 1107–1110, 1998.

McLeod, P., and R. S. J. Sparks, The dynamics of xenolith assimilation, *Contrib. Mineral. Petrol.*, 132, 21–33, 1998.

Paull, C. K., W. Ussler, and W. Dillon, Is the extent of glaciation limited by marine gas hydrate?, *Geophys. Res. Lett.*, 18, 432–434, 1991.

Rothwell, R. G., J. Thompson, and G. Kahler, Low-sea-level emplacement of a very large late Pleistocene 'megaturbidite' in the western Mediterranean Sea, *Nature*, 392, 377–380, 1998.

Sigurdsson, H., J. D. Devine, F. M. Tchoua, T. S. Presser, M. K. W. Pringle, and W. C. Evans, Origin of the lethal gas burst from Lake Monoun, Cameroon, *J. Volcanol. Geotherm. Res.*, 31, 1–16, 1987.

Sigvaldason, G. E., International Conference on Lake Nyos Disaster, Yaounde, Cameroon 16–20 March, 1987: Conclusions and recommendations, *J. Volcanol. Geotherm. Res.*, 39, 97–107, 1989.

Zhang, Y., Dynamics of CO_2-driven lake eruptions, *Nature*, 379, 57–59, 1996.

Zhang, Y., Experimental simulations of gas-driven eruptions: Kinetics of bubble growth and effect of geometry, *Bull. Volcanol.*, 59, 281–290, 1998a.

Zhang, Y., Energetics of gas-driven limnic and volcanic eruptions, *J. Volcanol. Geotherm. Res.*, 97, 215–231, 2000.

Zhang, Y., and Z. Xu, Bubble growth and dissolution on ascent in water: Applications to bubbles in beer and methane bubble dissolution in a water column, *Eos*, 82, S406, 2001.

Zhang, Y., and Z. Xu, Kinetics of convective crystal dissolution and melting, with applications to methane hydrate dissolution and dissociation in seawater, *Earth Planet. Sci. Lett.*, Submitted, 2003.

———————————

Y. Zhang, Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, USA. (youxue@umich.edu)