

## Methane-driven oceanic eruptions and mass extinctions: Comment and Reply

### COMMENT

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Brief intervals of profound global environmental change have punctuated Earth's history. During some of these times, including the Permian-Triassic boundary, the  $^{13}\text{C}/^{12}\text{C}$  ratio of carbonate and organic matter at numerous widespread locations decreased significantly ( $>2\%$ ). These negative  $\delta^{13}\text{C}$  excursions probably signify rapid and massive inputs of  $^{13}\text{C}$ -depleted carbon to the atmosphere and some to all portions of the ocean. Increasingly, methane has been implicated as the source of the  $^{13}\text{C}$ -depleted carbon, with most work suggesting a gas hydrate origin. Specifically, some environmental perturbation causing dissociation of gas hydrate in marine sediment to free gas bubbles, which then escape through sediment failure such as slumping (e.g., Katz et al., 1999). Recently, however, Ryskin (2003) has presented an alternative scenario whereby significant amounts of dissolved methane accumulated in stagnant deep waters and drove methane eruptions somewhat analogous to the carbon dioxide expulsions documented at Lake Nyos (e.g., Kling et al., 1987; Zhang, 1996). The purpose of this comment is to point out a basic problem with this model.

Ryskin (2003) suggests that methane solubility will steadily increase with depth in the ocean so that very high concentrations can accumulate in deep water and that free gas can exsolve from this water. Indeed, he states that the mole fraction of dissolved methane can reach  $\sim 4.3 \times 10^{-3}$  beneath 4 km of water. This view is incorrect because he has neglected the clathrate phase. Contrary to his assertion that "... it is immaterial whether some part of this methane flux results from dissociation of methane hydrates. . ." (p. 741), the ability of methane and water to crystallize as a clathrate at high pressure and low temperature necessarily complicates any scenario that invokes the buildup of methane in the deep ocean. Phase diagrams appropriate for understanding the methane-seawater system (Fig. 1) clearly show that the mole fraction of methane dissolved in water at 4 km depth cannot accumulate beyond  $\sim 1.2 \times 10^{-3}$ , otherwise the solid clathrate structure would precipitate. However, without the confines of sediment, deep waters of the ocean cannot store significant amounts of methane in methane hydrate because it floats. Initially, this may seem like a trivial point that merely drops the theoretical maximum for methane concentrations in the deep ocean, albeit significantly. However, as outlined by Ryskin (2003) and others (Zhang, 1996), gas eruptions occur when gas exsolves from solution, which decreases the density of a water parcel, which then causes the water parcel to rise, which releases additional gas. The formation of methane hydrate at relatively low methane concentrations necessarily precludes the exsolution of dissolved methane to free gas bubbles in deep water. Thus, a methane eruption cannot initiate from great depth. One might suggest that methane-driven eruptions could occur when large masses of floating gas hydrate rise into warm, shallow water and dissociate (Zhang, 2003). The enormous amount of methane required to cause a prominent negative  $\delta^{13}\text{C}$  anomaly would, however, necessarily mean that the floating gas hydrate was somehow dislodged from sediment beneath the seafloor.

### ACKNOWLEDGMENTS

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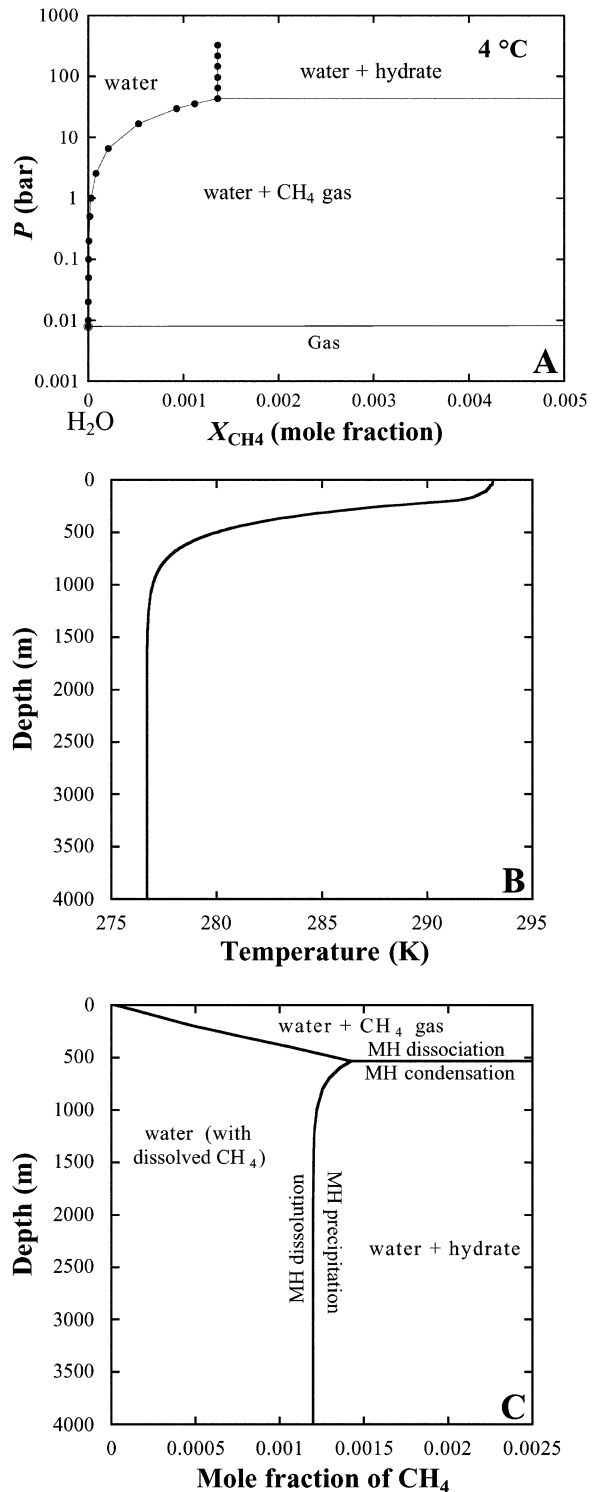


Figure 1. Diagrams pertinent to the methane-seawater system showing (A) methane phases with respect to pressure, (B) typical temperature profile in the ocean, and (C) expected phases with hydrostatic pressure gradient and  $4^\circ\text{C}$  deep water incorporated into the depth axis (adapted from Zhang and Xu, 2003). MH is methane hydrate.

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## REPLY

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Dickens raises an important question. Phase diagrams do not tell the whole story, however. (If they did, diamonds would have turned into graphite long ago; instead, they seem to last forever.) For methane in seawater, Handa (1990) calculated the metastable gas-liquid solubility (saturation solubility with respect to the gas phase), i.e., the concentration of methane in solution that would be in equilibrium with gaseous methane if hydrate did not form. In particular, for  $T = 5\text{ }^{\circ}\text{C}$  and  $P = 400\text{ bar}$ , he obtained  $4.3 \times 10^{-3}$  (mole fraction). Dickens argues that such concentrations are unattainable because hydrate crystals will precipitate from solution whenever the concentration of methane is higher than the one in equilibrium with hydrate,  $\sim 1.2 \times 10^{-3}$  (Handa, 1990). In the deep stagnant water column, this is far from certain because of the kinetic effects. Significant supersaturation of the solution relative to equilibrium with hydrate may be required for hydrate formation. Concentrations up to, or even above, the gas-liquid saturation solubility were required for hydrate formation in the experiments of Bishnoi et al. (1994), in spite of the presence of the gas phase. (Hydrate formation is greatly facilitated at the gas-water interface because the mole fraction of methane in hydrate,  $\sim 0.15$ , is much higher than the solubility of methane in water [Sloan, 1998].) In the absence of both the gas phase and the porous medium (the sediments), and with methane concentrations below the gas-liquid saturation solubility, precipitation of methane hydrate has never been achieved in the laboratory (as far as I know), and may not occur naturally at all.

More worrisome is the fact that the bubbles that transport methane from the seafloor to the water column are, apparently, covered with the hydrate “skin” (Rehder et al., 2002), in which case one would expect that the maximum concentration of dissolved methane around the bubble, and thus the maximum achievable in the water column, is the one in equilibrium with hydrate, not with free gas. This is a serious argument in favor of Dickens’ viewpoint. However, the skin cannot cover the bubble surface completely; if it did, its dissolution in the surrounding water could not be compensated by its reforming from the bubble side because there is no water inside the bubble. One possibility is that the upper part of the bubble’s surface, where the shear stress due to flow is the greatest, remains free of hydrate (G. Rehder, 2003, personal commun.; I. Leifer, 2003, personal commun.). This part is also where the mass transfer between the bubble and the liquid is most intensive; this may explain why the formation of the hydrate skin reduces the rate of bubble dissolution by only a factor of  $\sim 4$  (Rehder et al., 2002). Such “open top” bubbles could elevate the concentration of dissolved methane in the water column up to the gas-liquid saturation solubility. For present purposes, then, the existence of the hydrate skin on the bubbles may not be a limiting factor.

A definitive answer cannot be given before we understand how this skin forms and how it affects bubble dynamics and dissolution.

Another important consideration is that bubble plumes entrain and transport to the water column the gas-saturated water from below the seafloor (Leifer and Judd, 2002). This creates an additional delivery path for dissolved methane to the water column. Also, the geothermal heat flux, carried into the stagnant water column by the bubble plumes with their entrained water flow, and possibly by convection currents, should gradually increase the water column temperature, further reducing the likelihood of hydrate formation.

Perhaps the strongest evidence against Dickens’ argument is the observation that the hydrate stability zone in the sediments by no means forms an impermeable barrier for migration of methane-saturated water together with free gas (Ginsburg, 1998). According to one estimate, the amount of gas being converted into hydrate is less by five orders of magnitude than the amount passing through the hydrate stability zone without conversion (Ginsburg, 1998). Why the kinetics of natural hydrate formation is so slow is not completely understood.

The above discussion does not prove, of course, that methane can accumulate in the water column to concentrations close to the gas-liquid saturation solubility, but it does show that such accumulation cannot be ruled out on the basis of today’s knowledge.

The last sentence of the comment refers to the hydrate-dissociation model of the global perturbations of climate and of carbon cycle. In my view, this model finds little support in the data. Local releases of methane, associated with submarine slides, slope failures, etc., are obviously irrelevant to global events in the geological record. A global release of methane from the hydrate reservoir would require a global cause (deep-water warming or the like), so that hydrate dissociation itself must be explained by a climate event. (The cause of the latter has to be hypothesized in turn, and so on ad infinitum.) Dissociation would proceed from the base of the hydrate layer in the sediments, in most cases simply decreasing its thickness; only thin layers would melt entirely and release methane into the water column. Yet the amounts of methane required to produce significant carbon-isotope excursions in the geological record are in the range  $\sim 10^{18}$  to  $10^{19}$  g, i.e., may exceed the total amount of methane in hydrates. The recent estimates of the latter range from  $1.4 \times 10^{17}$  g (Soloviev, 2002) to  $3.6 \times 10^{18}$  g (Milkov et al., 2003).

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