A numerical model for the formation of gas hydrate below the seafloor

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ABSTRACT

We develop a numerical model to predict the volume and distribution of gas hydrate in marine sediments. We consider the environment of a deep continental margin where sedimentation adds organic material to the region of hydrate stability. Conversion of the organic material to methane by bacteria promotes hydrate formation and depletes the supply of organic carbon. We derive mass balance equations for the volume of hydrate and free gas bubbles in the sediments and account for the changing concentration of dissolved methane and salts in the pore fluid. The effects of sediment compaction and the associated fluid flow are explicitly modeled. Allowances for deeper sources of fluid are also described, though we focus on the case of an idealized passive margin where carbon is input solely through sedimentation.

INTRODUCTION

Large volumes of methane are sequestered in marine sediments along deep continental margins by an icy solid known as gas hydrate. Occurrences of gas hydrate are often indicated by the presence of a strong seismic reflection that parallels the seafloor [*Stoll et al., 1971; Shipley et al., 1979*]. The reflector is thought to coincide with the base of the region where hydrate is thermodynamically stable [*MacKay et al., 1994; Holbrook et al., 1996; Yuan et al., 1999*]. Several recent legs of the Ocean Drilling Program (ODP) have targeted known hydrate locations with the goal of characterizing marine gas hydrate [*Westbrook et al., 1994; Paull et al., 1996*]. The data collected from these studies provide a clearer picture of hydrate occurrences on both active and passive continental margins. On the basis of these data, attempts have been made to extrapolate local estimates of hydrate volume to infer a global inventory [*Kvenvolden, 1988a; Gornitz and Fung, 1993;*]. Empirical relationships between the hydrate volume and organic content in the sediments are typically used to estimate the global abundance of hydrate below the seafloor.

The need for more quantitative means of predicting hydrate accumulation in the world's ocean are threefold. First, by comparing model predictions with observations from known hydrate occurrences we have an opportunity to study the processes that are important for hydrate formation. Second, we can make better estimates of global abundances by improving our predictions of where hydrate should occur.   Finally, we can begin to quantify the role of gas hydrates in global climate change [*Kvenvolden, 1988b; Nisbet, 1990*]. Recently reported evidence of massive releases of methane in the Paleocene *[Dickens et al., 1997a; Norris and Rohl, 1999; Katz et al., 1999*] suggest that gas hydrate may have played an important role in the past.

MODEL

The model we present in this study differs from previously presented quantitative models in several important respects. First, we explicitly account for the concentration of dissolved methane in the pore fluid so that the rate of hydrate formation can be predicted in a thermodynamically consistent fashion. Second, we include a simple model for biological production of methane that depends on the available supply of organic carbon in the sediments. Conversion of organic material to methane by bacteria gradually depletes the carbon supply with time and limits the production of methane. This component of the model links the methane supply to the rate at which organic material is added through sedimentation. In this way we establish a testable connection between the geological conditions near the seafloor and the predicted characteristics of a hydrate occurrence. Figure 1 presents a typical model result obtained for the hydrate fraction and in situ chlorinity concentration using standard model parameters that include an organic carbon input of 1.5 % at the sea floor. An unexpected result of the model is the fact that both the hydrate fraction and chlorinity attain a steady state profile. Fluxes of methane into and out of the system become balanced once the steady state is reached. The existence of a steady state is important because it means that hydrate volume is not a good indication of accumulation time when methane is produced solely by in situ conversion of organic material. The hydrate profile is characterized by the increasing hydrate fraction with depth until its maximum at the base of the hydrate stability zone (HSZ). A sharp discontinuity occurs at the base of the hydrate stability zone due to the thermodynamic conditions (pressure-temperature) that render the hydrate structure unstable below this depth. The chlorinity profile shows an increase in freshening with depth and reaches a maximum freshening of 92 % to that of seawater, which is constant below the HSZ. This freshening observed below the HSZ is a direct result of the release of fresh water associated with the dissociation of hydrate as it is carried out of the stability zone by active sedimentation. The generation of hydrate and in-situ chlorinity profiles provides the opportunity to test the model results with data collected from the Ocean Drilling Program (ODP).

COMPARISON WITH OBSERVATIONS FROM ODP LEG 164

We test the model using observations from the Blake Ridge ODP Leg 164, where many of the model parameters are known. We find that the model predicts that the hydrate accumulation is unlikely to exceed an average pore volume fraction of 7 % in the absence of pervasive fluid migration. One of the most useful ODP measurements is the pore fluid chlorinity, which is obtained from recovered core samples. During recovery, hydrate in the pore volume dissociates and freshens the pore fluid. The amount of freshening is usually taken as a measure of the volume of hydrate that was present in the sediments before recovery. Quantitative estimates of the hydrate volume are routinely based on the assumption that the chlorinity of the pore fluid prior to the dissociation of hydrate is equal to that of seawater. Our numerical predictions of chlorinity indicate that this assumption is not strictly correct, but few options exist if the in situ chlorinity is not known. In our numerical model, however, we know the in situ chlorinity, so we can predict the pore fluid chlorinity that would be measured if a core sample were recovered. Very good correlation between the predicted and observed profiles of chlorinity is obtained (figure 2) when consumption of organic material by bacteria is confined to the uppermost region of sediments as. In particular, we find very good agreement through the top 200 m of the sediments and below 450 m. Between 200 m and 450 m the observations exhibit more scatter, but the trend is consistent with the prediction. The increased scatter in the observations does not necessarily mean that the measurements are less reliable. Our model predicts a smoothly varying distribution of hydrate through the sediments, but other processes may operate at the pore scale to redistribute hydrate into more massive forms [*Clennell et al., 1999*]. Such processes are not included in our model, but they could contribute to the scatter in the observations. Sediment cores with small nodules of solid hydrate would produce more freshening than sediments where the hydrate has been depleted. Our model predicts a dispersed distribution of hydrate, but it does not rule out a subsequent redistribution of hydrate about the predicted average. It is also possible that the observations are biased toward low hydrate volumes because samples with large volumes of hydrate may be disrupted during recovery during recovery by rapid decomposition. In extreme cases the sediments may be disrupted to such an extent that fluid samples cannot be collected. Loss of samples with high hydrate volume would bias the inferences of hydrate volume toward

lower values. This problem is expected to be most serious near the base of the HSZ, where the hydrate fractions are predicted to be largest. Overall, the numerical model reproduces the gross features of the chlorinity observations with a high degree of confidence and indicates that the production of methane through biogenic conversion of organic carbon is the key process operating on passive margins where pervasive fluid flow is not significant.

CONCLUSIONS

 We develop a quantitative model for predicting the volume and distribution of gas hydrate in marine sediments. The model is applied to a passive margin environment where methane is produced solely by in situ conversion of organic methane. Model results predict that the hydrate fraction is limited to a relatively small fraction of the pore volume in the absence of any upward fluid migration. For a total organic content of 1.5 % at the seafloor, it is unlikely that the hydrate occupies more than 7 % of the pore volume. Reports of larger volumes at active margins appear to require significant migration of methane-bearing fluids into the stability zone [*Hyndman and Davis, 1992*].

Model predictions for conditions that are representative of the Blake Ridge are compared with chlorinity measurements from ODP Leg 164. By making use of the predicted in situ variations in chlorinity, we obtain a very good match to the observed chlorinity profile. Our preferred estimate for biological productivity yields peak hydrate volumes when the sedimentation rate falls in the range commonly observed on deep continental margins (10 – 20 cm kyr^{-1}). The numerical calculations indicate that the key parameters in this model are the rate of sedimentation, the quantity and quality of the organic material, and a rate constant that characterizes the vigor of biological productivity. In general, the dependence of hydrate volume on these parameters is quite complicated, but the results can be readily applied to provide estimate global abundance and regions of hydrate occurrence using the best available data.

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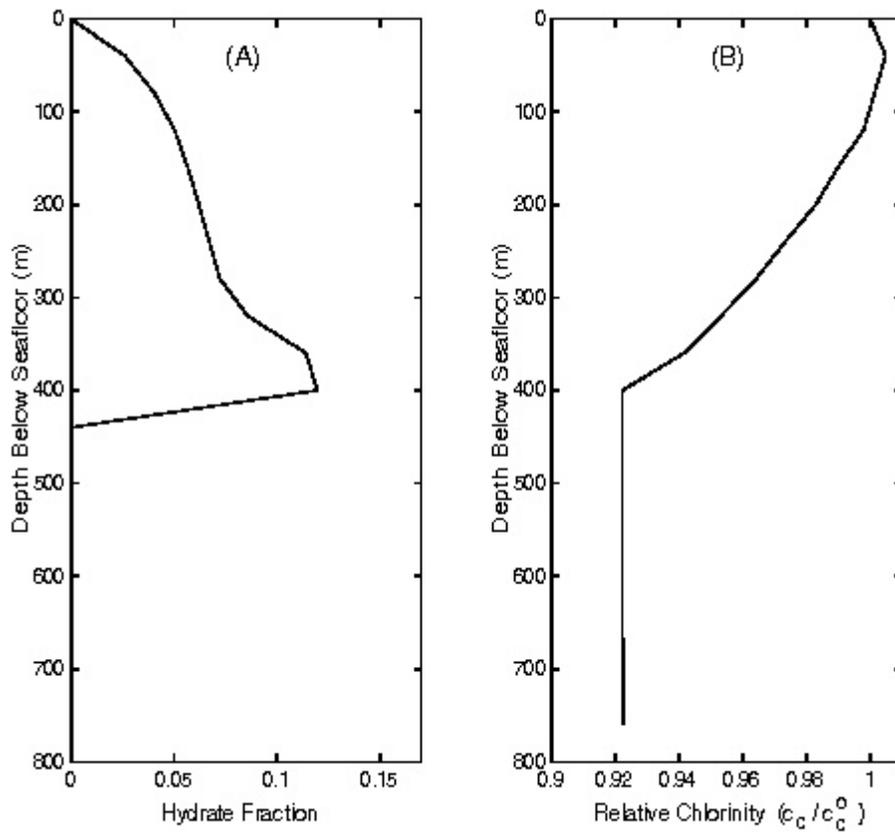
Figure 1: Predicted profiles of (a) hydrate volume and (b) relative chlorinity using a total organic carbon value of 1.5 %. The peak hydrate volume at the base of the HSZ is ~12 %. The chlorinity is less than the seawater value through most of the sediments. A slight excess chlorinity is produced near the seafloor due to vigorous hydrate formation in this location.
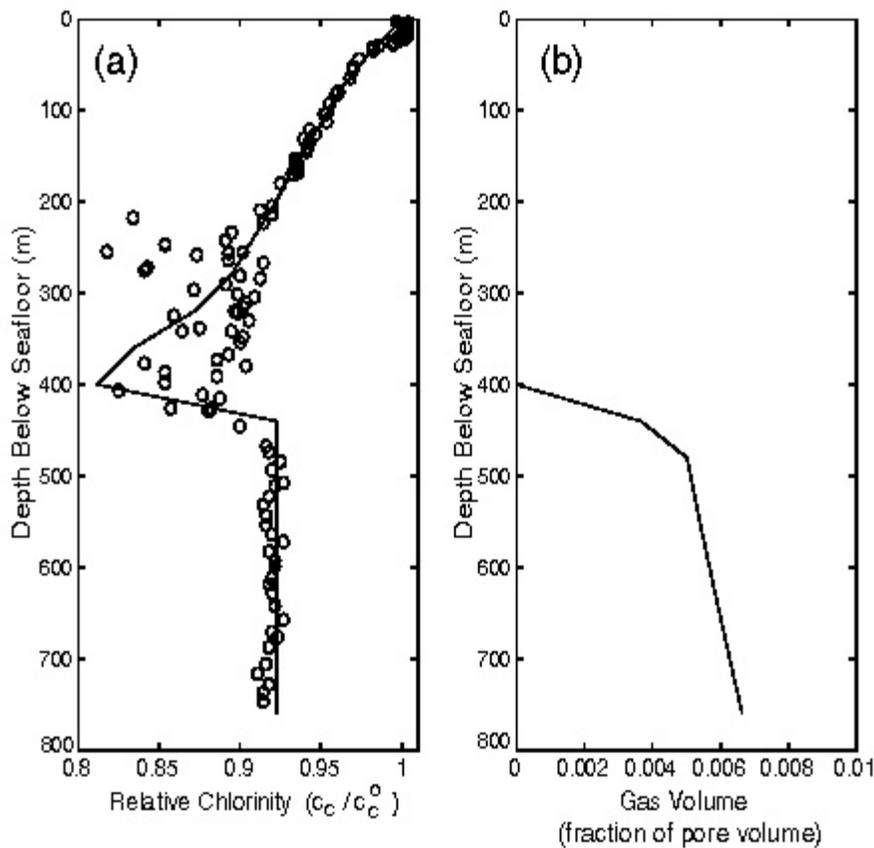
Figure 2: (a) Comparison of observed pore chlorinity at ODP Site 997 and predicted values calculated using model results for the hydrate fraction and in situ chlorinity. Good agreement is achieved in the top 200 m of sediments and below 400 m. The measurements exhibit greater scatter between 200 m and 400 m, but the trend is broadly consistent with predictions. (b) The volume of free gas predicted below the HSZ is ~0.6 % using the ideal gas law and pressure-temperature conditions characteristic of ODP site 997. Free gas volume is sensitive to the available organic carbon, and the rate constant that describes the conversion of organic carbon to methane. Increasing the available organic carbon can substantially increase the free gas fraction without significantly altering either the hydrate volume or the predicted chlorinity.