

## Chapter 3

© 2000 Kluwer Academic Publishers. All rights reserved.

# Practical Physical Chemistry and Empirical Predictions of Methane Hydrate Stability

**Edward T. Peltzer and Peter G. Brewer**

Monterey Bay Aquarium Research Institute  
Moss Landing, CA 95039

## 1. INTRODUCTION

### 1.1. Background

Accurate and precise prediction of the temperature and pressure (P-T) conditions at the boundary of the methane hydrate stability field is an essential component of a variety of endeavors in the field of geochemistry. Kvenvolden (1988), Gornitz and Fung (1994) and others have used knowledge of the P-T stability conditions to define the geophysical limits of gas hydrates and thereby estimate the size of the global reservoir. As the thermal signature of global warming penetrates into the ocean (Levitus et al., 2000), precise knowledge of the stability of gas hydrates will be required to assess the risks of decomposition in this reservoir. Recently, Ruppel (1997) has suggested that a discrepancy exists between *in situ* temperature measurements on the Blake Ridge and the predicted base of the hydrate stability zone. This claim is based in part upon P-T predictions of gas hydrate stability. In our own research, we have conducted a series of *in situ* deep-sea gas hydrate synthesis experiments (Brewer, et al., 1998) and have begun using an ROV to prospect for gas hydrate out-crops and undersea gas vents, which potentially result from decomposing gas hydrate deposits. One of the goals of this field work is to explore for gas hydrates close to the limit of the stability zone and this creates the need for accurate and precise predictions. Given the small temperature gradients with depth in the deep-sea, an error of 0.5°C, could mean a depth error of more than 100 meters. With a shallow sloping bottom (1% grade), one could easily be ten kilometers or more off target if the wrong temperature is used.

A variety of empirical P-T relationships for predicting the stability of methane hydrates can be found in the literature. The purpose of this chapter is not to provide an exhaustive list of these relationships nor to resolve all the discrepancies among them. This would be an injustice to the varied purposes of the studies and the authors involved. Nor do we pretend to present here a

complete description of the thermodynamics of gas hydrates. That has already been done in an excellent textbook by Sloan (1990, 1998), and the reader is referred there if a more complete understanding is desired. Rather, our goal is to select several representative approaches, to examine their differences, strengths and weaknesses, and to present some practical tools for applying these methods to the study of methane hydrates in the natural environment.

## 1.2. Ground rules for comparisons

In order to compare the various approaches to estimating the P-T conditions of methane hydrate stability, we need to establish both a level and consistent playing field. The need for this is obvious. A variety of units have been used in the literature for both pressure and temperature. To use all of them here would lead to much confusion. Additionally, chemists working in the lab prefer units of pressure on an absolute scale; geologists and oceanographers prefer to use a vertical depth scale in meters. While a simple conversion of depth to pressure has often been used, we will see shortly that this shortcut introduces systematic and detectable errors. While these errors were initially thought to be too small to be important, they are now becoming significant as the limits of precision and accuracy of both the measurements and the predictions are constantly being improved. Therefore, in the discussions that follow we will restrict ourselves to absolute pressure and temperature. Where necessary, the data has been converted to these units.

There are other reasons beyond simple clarity for adopting this approach. Methane hydrates experience pressure not depth. Thus it makes sense to use pressure. Additionally, because gravity varies with latitude, phase diagrams prepared using depth will vary tens of meters from site to site. While this may seem a small error at depths of several thousands of meters, it is at present well within our abilities to measure and can lead to false interpretations. Similar errors are introduced when the compressibility of seawater is not accounted for. Pressure at depth in the ocean is often measured relative to the sea surface as zero. Failure to correct for atmospheric pressure when converting to absolute pressure will give a pressure error which is equivalent to 10 meters in depth. A similar error is introduced if lab data is reported as gauge pressure and not absolute pressure. These errors are cumulative and yield pressure errors of 2 to 3 atmospheres which is equivalent to depth errors of about 20 to 30 meters.

The equations to convert gauge and *in situ* hydrostatic measurements to absolute pressure from laboratory experiments, oceanographic research and in deep-sea sediments, respectively, are:

$$P(\text{abs}) = P(\text{gauge}) + P(\text{atm}). \quad (1)$$

$$P(\text{abs}) = P(\text{water-column}) + P(\text{atm}). \quad (2)$$

$$P(\text{abs}) = P(\text{pore-water}) + P(\text{water-column}) + P(\text{atm}). \quad (3)$$

### 1.3. Converting depth to pressure

Typically, a constant density approximation has been made:

$$P(\text{at depth}) = \text{Depth}(\text{m}) \times \text{density} \times \text{acceleration of gravity}, \quad (4)$$

where, the density of the overlying water column is assumed to be 1.035 and the acceleration of gravity is  $9.8 \text{ m/s}^2$ . There are problems with this approach. Water is slightly compressible, so its density increases with depth. While small, the effect of this difference on pressure at depth is cumulative. The variation of gravity with latitude, makes this calculation site specific. These effects can be seen quite clearly in figure 1. Notice that below the seafloor, these effects work in reverse due to the geothermal gradient where pore-water temperature increases with depth. At higher temperatures, the density of the pore-water is greatly diminished and the cumulative pressure error can become negative.

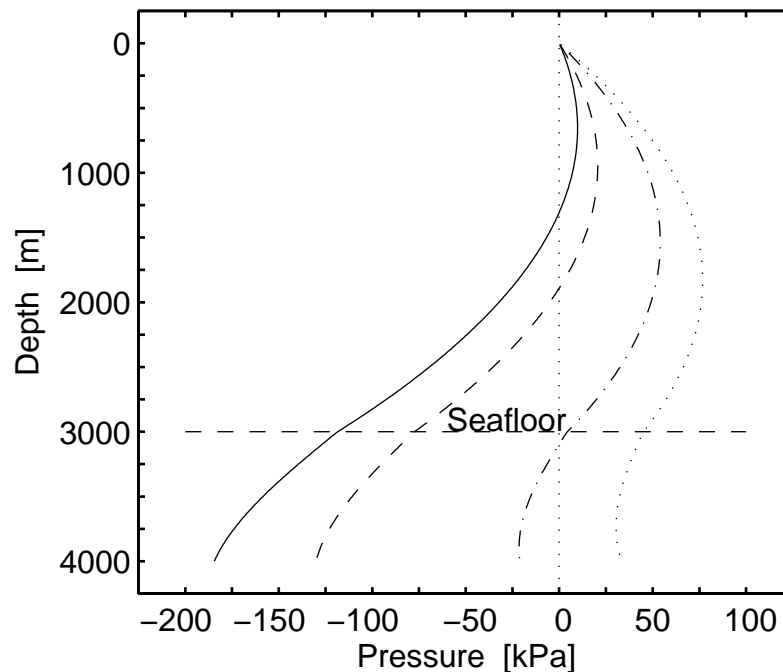


Figure 1. Calculated pressure differences vs depth between the simplified pressure relation and a calculation including the compressibility of seawater and the variation of gravity (Fofonoff and Millard, 1982) as a function of latitude (solid line,  $90^\circ$ ; dashed line,  $60^\circ$ ; dot-dash line,  $30^\circ$ ; and dotted line,  $0^\circ$ ). A standard ocean model was used: seawater salinity was 35 at a constant temperature of  $0^\circ\text{C}$ ; porewater salinity was 32.5 and the geothermal gradient in the sediments was  $35^\circ\text{C}/\text{km}$ . Note that one atmosphere equals 101.3 kPa, which is equivalent to about 10m in depth.

## 2. P-T CONDITIONS OF METHANE HYDRATE STABILITY

### 2.1. Types of estimates

It would be a very large task to experimentally measure the P-T conditions for the boundary of the methane hydrate stability field at all of the possible combinations of temperature, pressure and salinity of interest to geochemists. Thus, various means to estimate these parameters have been developed and these methods fall into two types. The first type estimates the P-T relationship for the boundary by interpolating between experimentally determined dissociation data. Various equations have been fit. In some cases seawater data was available; in other cases freshwater data was used and the dissociation temperatures were adjusted for the effects of sea-salt. The second type of predictions are made based upon minimizing the Gibbs Free Energy of the system. These calculations have the advantage that both salinity and gas compositions can be freely varied.

### 2.2. Data Interpolations

Dickens and Quinby-Hunt (1994) were the first to make measurements of methane hydrate stability in seawater, and they fit a linear equation to their data:

$$1/T = 3.79 \times 10^{-3} - 2.83 \times 10^{-4} \log_{10}P, \quad (5)$$

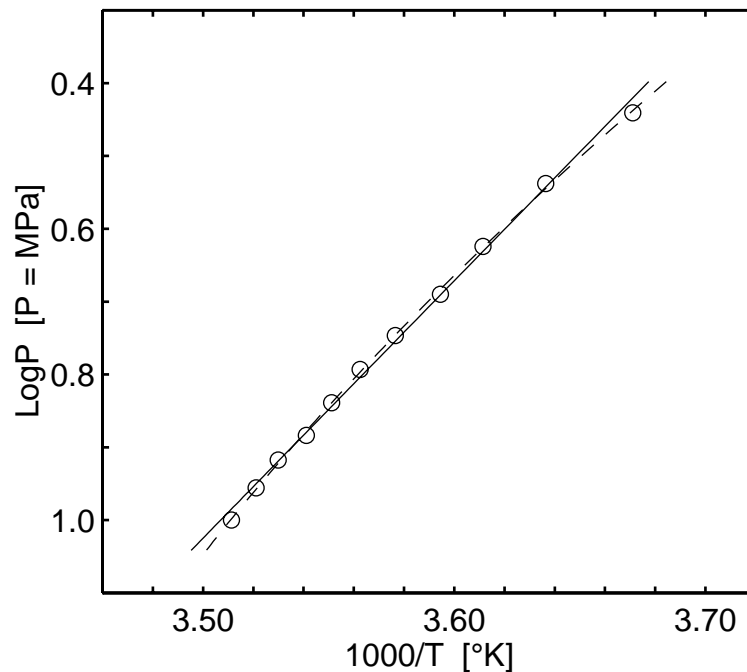


Figure 2. Plot of methane hydrate in seawater stability data (o) from Dickens and Quinby-Hunt (1994); their linear fit (—) to equation (5) and the second order polynomial fit (---) to equation (7). Curvature in the data is apparent for even this small range.

where,  $T$  is in degrees K and  $P$  is pressure in MPa (Fig. 2). This relationship is based upon the Clausius-Clapeyron equation:

$$d(\ln P) / d(1/T) = -\Delta H / zR, \quad (6)$$

where  $\Delta H$  is the enthalpy of formation,  $z$  is the compressibility and  $R$  is the gas constant. Sloan (1990, 1998) has pointed out that this equation predicts straight lines over limited temperature ranges (assuming  $\Delta H$  and  $z$  are constant). This statement raises the obvious questions, what is the extent of this limited temperature range, and how straight is straight? Fitting a simple second order polynomial to their data we obtain:

$$1/T = 3.83 \times 10^{-3} - 4.09 \times 10^{-4} \log_{10}P + 8.64 \times 10^{-5} (\log_{10}P)^2. \quad (7)$$

This equation reveals significant curvature for even this limited temperature range (Fig. 2). When plotted in linear temperature vs pressure space, the offset between the data and equation (5) becomes more apparent (Fig. 3).

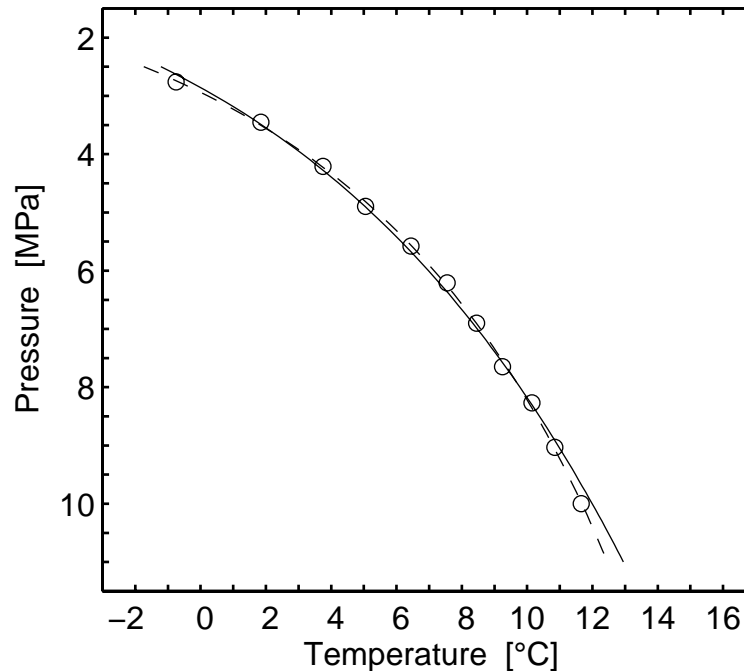


Figure 3. Plot of data from Dickens and Quinby-Hunt (1994) in linear temperature and pressure space; the linear fit (—) to equation (5) and the second order polynomial fit (---) to equation (7) are also shown. Although the offset between the linear fit and the data is small ( $<0.5^{\circ}\text{C}$ ), it is poorest at the ends of the line as well as at the mid-point of the data.

Extrapolation of these equations to higher P-T conditions reveals an ever increasing discrepancy between them (Fig. 4). After converting pressure to depth, and thereby introducing the error due to variations in gravity with latitude, Brown et al. (1996) fit the data of Dickens and Quinby-Hunt (1994) to a different second-order polynomial and obtained the following equation:

$$T = 11.726 + 20.5 \times \log_{10}z - 2.2 \times (\log_{10}z)^2, \quad (8)$$

where, T is temperature in degrees C and z is depth in kilometers. This equation is also plotted in figure 4 after adjusting depth back to pressure, etc. Without data on the stability of methane hydrates in seawater at high temperature and pressures, it is impossible to tell which equation (5, 7 or 8) is correct. Dickens and Quinby-Hunt (1994, 1997) have found that there is a 1.1 – 1.2°C difference between the predictions for methane hydrate in pure water and seawater of 33.5 salinity at equivalent pressures. Handa (1990) fit the stability data for methane hydrates in pure water at 0.2 to 40 Mpa to obtain:

$$\ln(P/P_0) = -1205.907 + 44097.00 / T + 186.7594 \ln T, \quad (9)$$

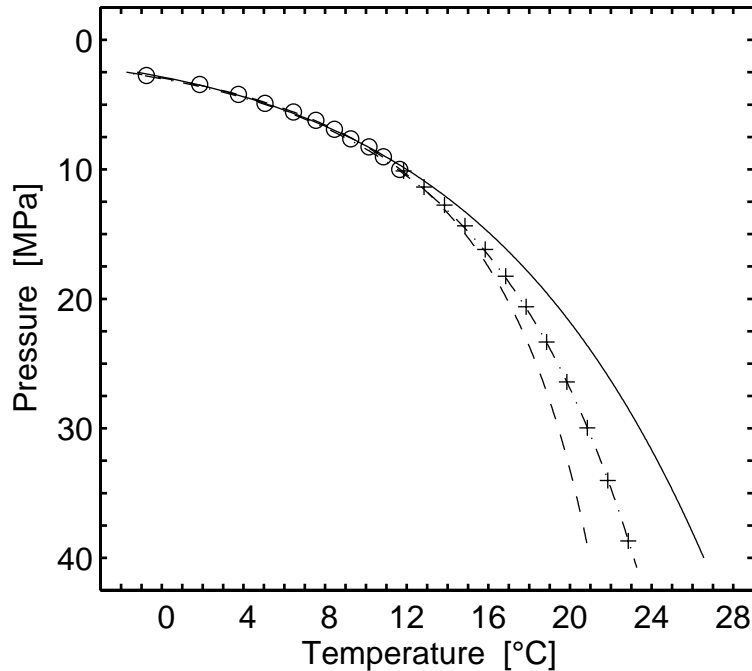


Figure 4. Plot of the linear fit (Eq. 5, —), the second-order polynomial fit (Eq. 7, - - -) and equation 8 converted to absolute pressure (- · - ·). Also shown is the stability data for methane hydrate in seawater (o) from Dickens and Quinby-Hunt (1994) and the freshwater stability data calculated at 1°C intervals with equation 9 offset by 1.15°C (+) to adjust for the destabilizing effects of sea-salt.

where  $T$  is in degrees K and  $P_0 = 1.01325$  bar. Applying the mean offset to equation (9) for methane hydrate stability in pure water, allows us to test these three predictions at higher pressures (Fig. 4). Clearly, equation (8), when converted to pressure, is the closest extrapolation to the freshwater data from equation (9) adjusted to seawater.

### 2.3. Gibbs Free Energy Minimizations

Several methods to estimate the P-T conditions of methane hydrate stability by searching for the state which minimizes the Gibbs Free Energy of the system have been developed. These programs are computationally intensive and require sophisticated computer programming. However, computer programs to carry-out these calculations are now readily available. Sloan (1990, 1998) presents a detailed description of CSMHYD, a PC-DOS based computer program. His textbook includes a floppy disk with an executable version of the program. In addition to calculations of the stability temperature at a given pressure (or vice-versa) in pure water, the program also includes a variable composition salt component to allow seawater and pore-water predictions. We refer the reader to the textbook for the details of how the program works. Output from CSMHYD is shown in figure 5 for a pure methane hydrate in equilibrium

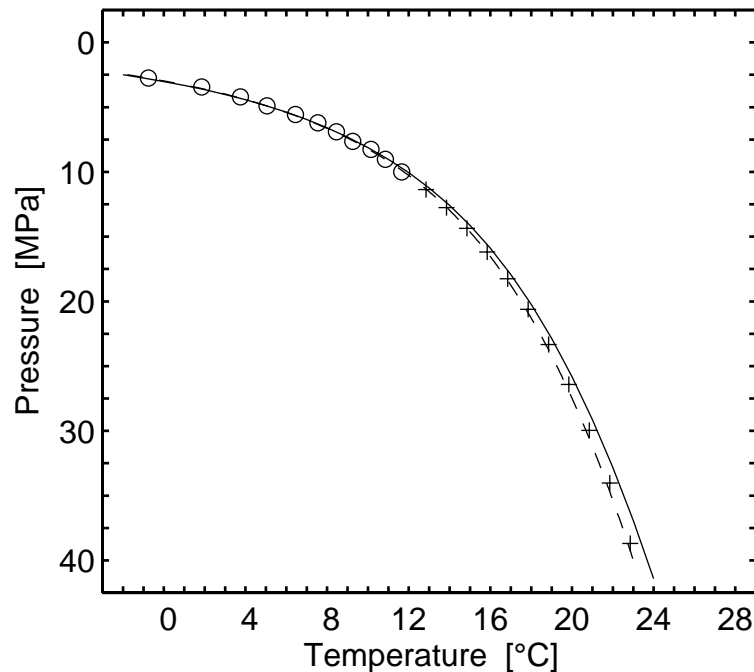


Figure 5. Output from CSMHYD (—) and Multiflash (---) plotted with the seawater data (o) from Dickens and Quinby-Hunt (1994) and the predictions from equation (9) offset for seawater (+) as in Figure 4.

with seawater. A salinity of 33.5 was chosen for the CSMHYD predictions so that a direct comparison could be made with the seawater data and the stability conditions calculated using equation (9) and adjusted to seawater, as above in figure 4. Clearly, the CSMHYD predictions better fit with the seawater data than the freshwater predictions adjusted to seawater at  $P > 12\text{MPa}$ .

Zatsepina and Buffet (1997, 1998) present an alternate Gibbs Free Energy minimization routine based, in part, on a very fast simulated annealing algorithm (Ingber, 1989). Their results are quite similar to the CSMHYD program and compare favorably to a prediction from Handa (1990). Recently, they have begun exploring whether the equilibrium calculations are sufficient or whether additional complexities lay in meta-stable phases that persist in nature outside their stability fields as decomposition of the gas hydrate is impeded by the free energy required to create small bubbles (Buffet and Zatsepina, 1999).

A commercially available program, Multiflash (Infochem Computer Services Ltd., London), also calculates the P-T conditions for methane hydrate stability using the Gibbs Free Energy minimization approach. It is more sophisticated than CSMHYD, running in the Windows® operating system, and it performs a wider variety of calculations. The Multiflash P-T predictions for methane hydrate stability in seawater of salinity 33.5 are also shown in figure 5. They are slightly different from the CSMHYD program and compare quite favorably with both the seawater data and the higher P-T predictions from equation (9) adjusted to seawater as before.

Given the close correspondence between these computer programs and the predictions based upon equations (8) and (9), it is logical to ask why incur the additional expense of the programs if the equations work so well? For pure methane hydrates in freshwater or seawater of salinity 33.5, these equations are the simplest approach. However, if one is dealing with substantially different salinity, or different salt compositions, as may be found in pore-water, or with mixed gas compositions, then computer programs offer the ability to deal with these situations and to extend the predictions beyond the range of the data. This can be seen quite clearly in figure 6, where the differences between the predicted equilibrium P-T conditions for mixed gas hydrate stability in salinity 33.5 seawater, where the gas is a composite of methane and other natural gases, and pure methane hydrate in the same salinity seawater are plotted as a function of pressure. For this example, we progressively increased the complexity of the gas mixture, starting with methane + ethane, then adding carbon dioxide and hydrogen sulfide (see the figure caption for the percent composition). These differences (0.4-2.0°C) are larger than the effects described earlier and they vary with pressure. Also shown is the destabilizing effect of high salinity (40.0) on pure methane hydrate. These lines represent complex functions for which it will be difficult to derive simple mathematical expressions. Thus, it is in situations that address the complex real-world problems of mixed gas compositions and varied salinity that the computer programs will find their greatest use.

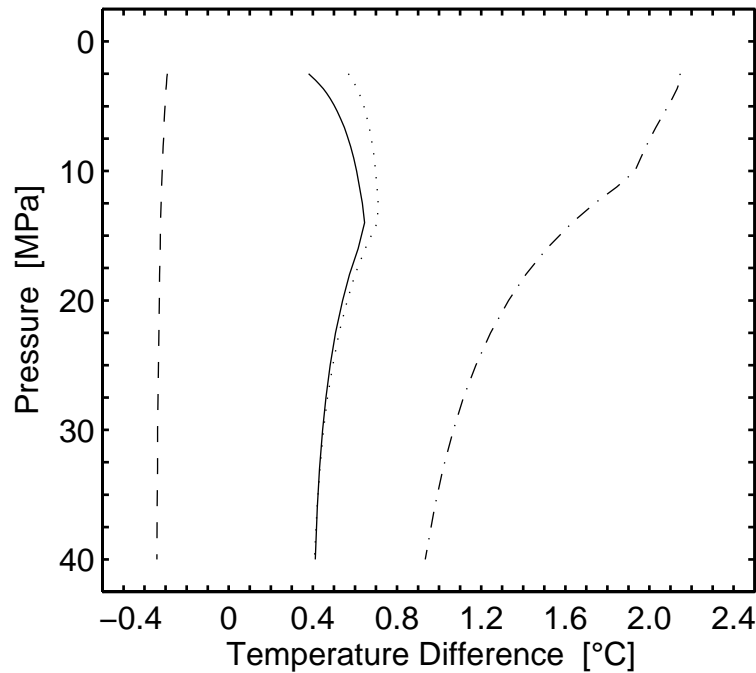


Figure 6. Plot of the temperature differences as a function of pressure between the Multiflash predictions for methane hydrate stability in high salinity (40.0) seawater (---); and methane + 2% ethane (—), methane + 2% ethane + 2% CO<sub>2</sub> (····), and methane + 2% ethane + 2% CO<sub>2</sub> + 2% H<sub>2</sub>S (— · —) in seawater of salinity 33.5 relative to pure methane hydrate in seawater of salinity 33.5, respectively.

### 3. TWO REAL WORLD EXAMPLES

#### 3.1. Eel River Basin

Brooks et al. (1991) reported the presence of gas hydrates (>99% CH<sub>4</sub>) in sediment cores collected near the crest of a large sedimentary ridge in the Eel River basin off the coast of northern California. When this site was revisited with the MBARI ROV *Ventana* in 1997 and in 1999, no gas hydrates were found in the shallow sediment cores collected but several active gas vents were observed on both occasions. A temperature increase of 0.4–0.5°C was observed for the bottom water between the time when Brooks et al. (1991) collected their samples and our investigations. In order to determine whether this small change in bottom water temperatures was the reason that no gas hydrates were found, despite the presence of abundant free methane gas, we plotted the relevant hydrographic data on the methane hydrate phase diagram (Fig. 7). Given sufficient methane concentrations, hydrates would be stable in the region to the left and below the stability line. The bottom-water temperature observed by Brooks et al. (1991) when plotted at the appropriate temperature clearly falls within this region; whereas the temperature we observed does not. Thus, for a

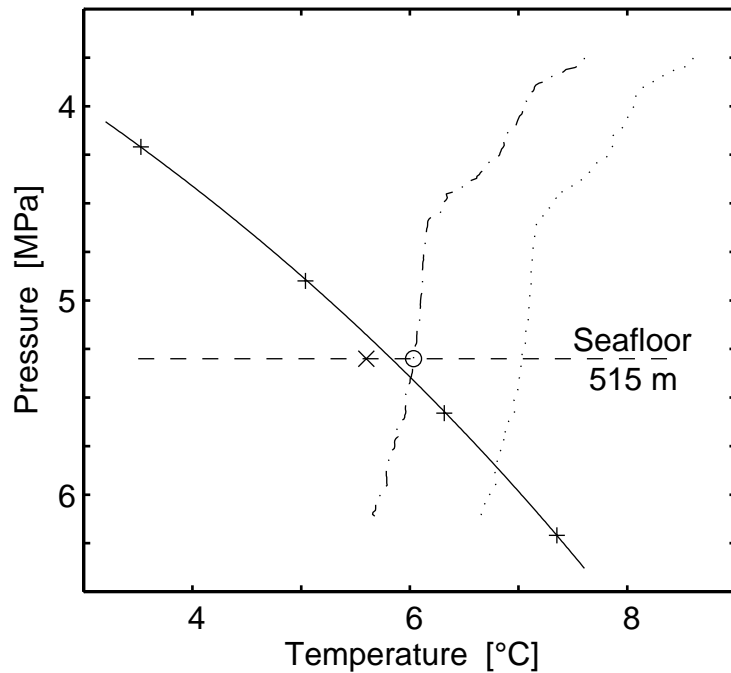


Figure 7. P-T stability curve for methane hydrate in seawater from equation 7 (—) and selected prediction using Multiflash (+). Bottom water temperatures from by Brooks et al. (1991) (x) and the authors (o). The *in situ* temperature profile nearby the dive site (---) and offset 1°C (···).

first cut at an explanation, it would appear that the simple thermodynamic stability of methane hydrates explains why no gas hydrates were collected. It is not possible to say at this early stage whether the warming we observed at this site since Brooks et al. (1991) collected their samples is due to global warming or whether a more localized explanation is possible. Even so, if we shift the observed temperature profile 1°C, the potential impact of even a modest amount of warming on the stability of gas hydrate deposits is evident. At present, the temperature profile crosses the stability curve for methane hydrate at 5.41 MPa, equivalent to 526 m depth – ten meters into the sediments near the crest of the ridge. When shifted, the temperature profile crosses the stability curve at 5.86 MPa, equivalent to 571 m. This is an increase of 45 m. If such a shift in seawater temperature were to occur instantaneously, there would be a lag time before the thermal effect penetrated deep into the sediments. However, as it does, any existing gas hydrates within this zone would eventually decompose, releasing methane gas and water. Whether this is sufficient to destabilize the sediments and cause seafloor collapse remains to be seen.

### 3.2. Blake Ridge

Recently, Ruppel (1997) has pointed-out that when the *in situ* temperature gradient and the stability boundary for methane hydrate are plotted together, the geotherm and the stability boundary do not intersect at the depth of the bottom-simulating reflector (BSR) for several sites on the Blake Ridge. Since the BSR is considered to be at or near the top of the free gas zone, it is often considered to represent the base of the hydrate stability zone (Markl et al., 1970). The fact that it does not presents an interesting geochemical conundrum. This problem persists even after all the data are corrected to absolute pressure and the appropriate P-T stability conditions are calculated (Fig. 8). At first glance, it is easy to suggest that the problem lies in the geothermal gradient chosen by Ruppel (1997) since the geothermal gradient reported in *The Initial Reports of the ODP, Leg 164* nicely intersects the stability line near the depth of the BSR. However, this conclusion is inappropriate. The geothermal gradient used by Ruppel (1997) is anchored by a measurement only 50 m above the BSR, whereas the ODP geothermal gradient was anchored at the sea-floor. Given that both are extrapolations, it would be best to measure the *in situ* temperature at the

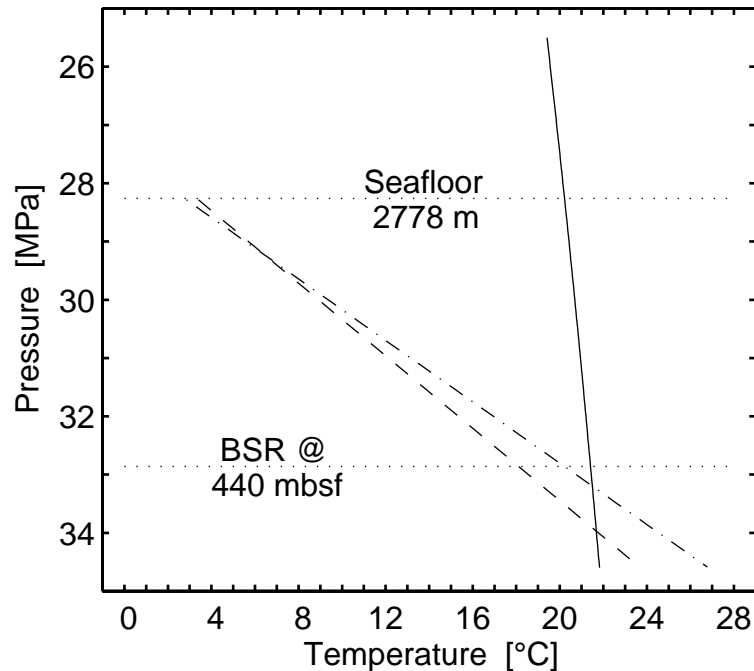


Figure 8. Temperature and pressure conditions for DSDP Site 995 on the Blake Ridge. Equilibrium stability conditions were calculated with Multiflash (—); the thermal gradients of 32.7°C/km (----) and 38.6°C/km (-.-.-) are from Ruppel (1997) and the Initial Reports from ODP Leg 164.

BSR since there are no guarantees that the geothermal gradients must remain constant. Indeed, given that the BSR may coincide with a phase change, we should expect to find, at the very least, a change in the geothermal gradient in the region of the BSR. At the same time, given the effects that we saw earlier (Fig. 6), the importance of *in situ* measurements of the pore-water salinity, gas composition and pressure regarding predictions of the P-T stability conditions at this site can not be over-stated. Only then can we determine whether sufficient methane is present in the pore-spaces to achieve saturation relative to methane hydrate solubility (Xu and Ruppel, 1999). At present, the conundrum exists because of conflicts among extrapolations, not *in situ* observations; and it is only through additional observations that the solution to the riddle will be found.

#### 4. SUMMARY AND CONCLUSIONS

Accurate and precise predictions of the temperature and pressure (P-T) conditions for the methane hydrate stability field have been shown to be an essential component of a variety of geochemical efforts. Careful correction of all measurements to absolute pressure is essential if a precision equivalent to a few meters depth is required. While linear interpolation of gas hydrate stability data works well in limited cases, second-order equations do a better job with regards to interpolating between existing data points. Our current inventory of geochemically relevant determinations of the dissociation temperatures and pressures of gas hydrates is very limited. Only one data set for seawater exists, and this is limited to pure methane gas measurements. Depending upon the form of the equation chosen to fit this data set, extrapolations to higher P-T conditions can be quite risky and lead to false interpretations. Adjustment of high pressure freshwater measurements can help extend the database, but these measurements are limited to pure methane gases as well.

The use of computer routines based upon various Gibbs Free Energy minimization algorithms to estimate the P-T stability conditions of gas hydrates has helped to expand the range of the predictions, but data to verify these estimates is quite scarce. Agreement between the computer predictions and the existing data is quite good, suggesting that the programs are accurate within reasonable limits. Their greatest utility will be with problems involving mixed gas compositions or at different salinities and ionic strengths not found in the data sets.

#### 5. ACKNOWLEDGEMENTS

The authors would like to thank Jerry Dickens, Keith Kvenvolden, Charlie Paull, Carolyn Ruppel and Bill Ussler for helpful discussions and critical comments. This work was supported by a grant to the Monterey Bay Aquarium Research Institute by the David and Lucile Packard Foundation.

## 6. REFERENCES

- Brewer, P.G., Orr, F.M., Friederich, G., Kvenvolden, K.A., & Orange, D.A. 1998. Gas hydrate formation in the deep sea: in situ experiments with controlled release of methane, natural gas, and carbon dioxide. *Energy & Fuels* 12, 183-188.
- Brooks, J.M., Field, M.E. & Kennicutt, M.C. 1991. Observations of gas hydrates in marine sediments, offshore northern California. *Marine Geology* 96, 103-109.
- Brown, K.M., Bangs, N.L., Froelich, P.N. & Kvenvolden, K.A. 1996. The nature, distribution, and origin of gas hydrate in the Chile Triple Junction region. *Earth and Planetary Science Letters* 139, 471-483.
- Buffett, B.A. & Zatsepina, O.Ye. 1999. Metastability of gas hydrate. *Geophysical Research Letters* 26, 2981-2984.
- Dickens, G.R. & Quinby-Hunt, M.S. 1994. Methane hydrate stability in seawater. *Geophysical Research Letters* 21, 2115-2118.
- Dickens, G.R. & Quinby-Hunt, M.S. 1997. Methane hydrate stability in pore water: a simple theoretical approach for geophysical applications. *Journal of Geophysical Research* 102, 773-783.
- Fofonoff, N.P. & Millard, R.C. 1982. Algorithms for computation of fundamental properties of seawater. *UNESCO Technical Papers in Marine Science* 44, 25-28.
- Gornitz, V., & Fung, G.W. 1994. Potential distribution of methane hydrates in the world's ocean. *Global Biogeochemical Cycles*, 8, 335-347.
- Handa, Y.P. 1990. Effect of hydrostatic pressure and salinity on the stability of gas hydrates. *Journal of Physical Chemistry* 94, 2652-2657.
- Kvenvolden, K.A. 1988. Methane hydrate - a major reservoir of carbon in the shallow geosphere? *Chemical Geology*, 71, 41-51.
- Levitus, S., Antonov, J.I., Boyer, T.P. & Stephens, C. 2000. Warming of the world ocean. *Science*, 287, 2225-2229.
- Markl, R.G., Bryan, G.M. & Ewing, J.I. 1970. Structure of the Blake-Bahama outer ridge. *Journal of Geophysical Research* 75, 4539-4555.

- Ruppel, C. 1997. Anomalously cold temperatures observed at the base of the gas hydrate stability zone on the U.S. Atlantic passive margin. *Geology*, 25/8, 699-702.
- Sloan, E. Dendy. 1990. *Clathrate hydrates of natural gases*. Marcel Dekker, Inc., New York.
- Sloan, E. Dendy. 1998. *Clathrate hydrates of natural gases*, second edition, revised and expanded. Marcel Dekker, Inc., New York. 705pp.
- Xu, W. & Ruppel, C. 1999. Predicting the occurrence, distribution, and evolution of methane gas hydrate in porous marine sediments. *Journal of Geophysical Research* 104, 5081-5096.
- Zatsepina, O.Ye & Buffett, B.A. 1997. Phase equilibrium of gas hydrate: implications for the formation of hydrate in the deep sea floor. *Geophysical Research Letters* 24, 1567-1570.
- Zatsepina, O.Ye & Buffett, B.A. 1998. Thermodynamic conditions for the stability of gas hydrate in the seafloor. *Journal of Geophysical Research* 103, 24,127-24,139.