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20. DETERMINATION OF IN SITU METHANE BASED ON ANALYSIS OF VOID GAS[1]

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ABSTRACT

A method for quantifying in situ dissolved methane concentrations in sediment cores that have gas voids is described. The method relies on normalizing methane (CH_4) in the gas voids to nitrogen (N_2) and/or argon (Ar). The principles of the method are presented. The method was tested during Ocean Drilling Program Leg 201, and preliminary results indicate that it can be used to generate reproducible and accurate dissolved methane values if argon and nitrogen are both measured or if one is measured along with pressure of the gas void.

INTRODUCTION

Methane (CH_4) is a major product of subseafloor microbial metabolic activity, and quantification of its abundance in sediments is necessary to understand subseafloor biology and biogeochemistry (Martens and Berner, 1974). However, often it is not possible to accurately determine in situ abundances by the standard technique of sediment headspace analysis (Kvenvolden and McDonald, 1986). This problem occurs when gas voids form during core retrieval and sampling, stripping CH_4 from the pore fluid. The formation of gas voids can occur when the total gas pressure exceeds the confining pressure within the core liner. Thus, as confining pressure decreases during core retrieval and sampling, gas voids and bubbles commonly collect within the liners of cores recovered from sediments with high CH_4 concentrations. The pressure core

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sampler (PCS) was designed to overcome this problem and quantify the abundance of methane hydrates by recovering sediments under in situ pressure (Pettigrew, 1992).

A principal aim of Ocean Drilling Program (ODP) Leg 201 was the examination of microbial activity in sediments that included those with high methane abundances and generated gas voids on recovery (D'Hondt, Jørgensen, Miller, et al., 2003). The PCS was deployed successfully during Leg 201; however, its use requires significant drilling and processing time (Dickens et al., 2003). Here we present the basis for and preliminary tests of an alternative method for the quantification of CH_4 in gas-rich sediments that does not require significant additional drilling or processing time.

THEORY OF METHOD

In this procedure, dissolved CH_4 concentrations are determined by normalizing measured gas void CH_4 to another gas, such as N_2 or Ar, that is stripped from the pore fluid but whose in situ concentration is known. The in situ concentrations of the normalizing gases are assumed to be established by atmospheric equilibrium at the temperature at which local bottom water formed. These gases are assumed to be unreactive in sediments. Claypool and Threlkeld (1983) considered a method based on normalization to CO_2.

Although it is unequivocal that Ar is unreactive, N_2 pore fluid concentrations can be influenced by microbially mediated denitrification and nitrogen fixation. It is unlikely, however, that nitrogen fixation occurs in deeply buried marine sediments, as there is always dissolved ammonium available and the quantitative importance of denitrification is limited because the dissolved nitrate concentration in deep ocean waters is at most less than ~5% of that of dissolved N_2 (Pilson, 1998).

Because the molar ratios of CH_4, N_2, and Ar in gas voids may differ from that in solution, we first develop theoretical relationships between the in situ dissolved CH_4 concentration, $[CH_4]^0$, the measured vapor phase mole fractions of CH_4, N_2, and Ar in gas voids (X_{CH4}, X_{N2}, and X_{Ar}, respectively), and the in situ dissolved inert gas concentrations. Relationships are separately presented for three procedural variations depending on what is measured: (1) when only the gas phase mole fractions of CH_4 and one inert gas are determined, (2) when total vapor phase pressure of the gas void along with the gas phase mole fractions of CH_4 and one inert gas are determined, and (3) when the gas phase mole fractions of CH_4, N_2, and Ar are determined. The additional measurements in procedures 2 and 3 remove one source of uncertainty implicitly associated with procedure 1. We also address uncertainties related to corrections that account for sample contamination due to the entrainment of ambient air during sampling.

Fractionation of the dissolved gases between the vapor phase and the aqueous phase will occur during the ebullition of gases from the sediment during decompression and warming on deck due to differences in solubilites and diffusivities; dissolved gas molar ratios are not necessarily identical to gas void molar ratios. The relationships we develop for calculating $[CH_4]^0$ assume that fractionation is dominantly due to differences in solubility rather than diffusivity. This assumption is justified by the consideration of the dynamics of bubble growth (see the **"Appendix,"** p. 9).

With these assumptions we develop two models of vapor-phase formation that can be considered as physical end-members that describe the distribution of gas between pore fluid and gas voids: (1) equilibrium vapor phase degassing and (2) fractional vapor phase degassing. Because it is unclear which model more closely represents how gas is distributed, the uncertainty in calculated $[CH_4]^0$ due to the choice of degassing model is considered.

The equations that are derived for both models follow from mass balance. That is, the initial number of moles of gas in a volume of pore fluid is set equal to the sum in pore fluid and gas void following degassing. Additionally, Henry's law and ideal gas behavior are assumed.

In equilibrium degassing, it is assumed that there is chemical equilibrium between the entire vapor phase and the degassing fluid. The mass balance for each gas (ignoring the small amount of water in the vapor phase) is given by

$$M_{\mathrm{iw}} C_{\mathrm{i}}^{0} = [V_{\mathrm{vapor}}(X_i P/\mathrm{R}T) + M_{\mathrm{iw}} C_{\mathrm{i}}], \tag{1}$$

where

R = gas constant,
P = total pressure of the gas phase,
T = temperature (K),
V_{vapor} = volume of the vapor phase,
M_{iw} = mass of interstitial water,
$\mathrm{X_i}$ = gas phase mole fraction,
C_{i}^{0} = dissolved gas concentration of i in situ, and
C_{i} = dissolved gas concentration of i following gas void formation.

Applying Henry's law,

$$C_{\mathrm{i}}^{0} = [(V_{\mathrm{vapor}}/M_{\mathrm{iw}}\mathrm{R}T) + K_{\mathrm{H}}^{\mathrm{i}}]X_{\mathrm{i}}P, \tag{2}$$

where

$K_{\mathrm{H}}^{\mathrm{i}}$ = Henry's law constant for species i.

Substituting $[CH_4]^0$ and an inert gas, I, for C_{i}^{0} and eliminating P, the relationship between $[CH_4]^0$ and the vapor phase molar ratio, $X_{\mathrm{CH4}}/X_{\mathrm{I}}$, is then given by

$$[\mathrm{CH_4}]^0 = (X_{\mathrm{CH4}}/X_{\mathrm{I}})\{[K_{\mathrm{H}}^{\mathrm{CH4}} + (V_{\mathrm{vapor}}/M_{\mathrm{iw}}\mathrm{R}T)]/[K_{\mathrm{H}}^{\mathrm{I}} + (V_{\mathrm{vapor}}/M_{\mathrm{iw}}\mathrm{R}T)]\}[\mathrm{I}]^0. \tag{3}$$

In the case of fractional degassing it is assumed that the vapor is no longer in contact with the fluid after it is released and each gas is in equilibrium with the fluid at the time it degassed. In this case, C_{i} varies with degassing as

$$(\mathrm{d}C_{\mathrm{i}}/\mathrm{d}V_{\mathrm{vapor}}) = -(X_{\mathrm{i}}P/M_{\mathrm{iw}}\mathrm{R}T) = -(C_{\mathrm{i}}/K_{\mathrm{H}}^{\mathrm{i}}M_{\mathrm{iw}}\mathrm{R}T). \tag{4}$$

Solving for C_{i} and applying mass balance (equation 1) leads to

$$C_{\mathrm{i}}^{0} = (PX_{\mathrm{i}}V_{\mathrm{vapor}}/M_{\mathrm{iw}}\mathrm{R}T)\{1 - \exp[-(V_{\mathrm{vapor}}/M_{\mathrm{iw}}\mathrm{R}TK_{\mathrm{H}}^{\mathrm{i}})]\}. \tag{5}$$

Thus, $[CH_4]^0$ is related to the vapor phase molar ratio $X_{\mathrm{CH4}}/X_{\mathrm{I}}$ and $[\mathrm{I}]^0$ by

$$[CH_4]^0 = (X_{CH4}/X_I)(\{1 - \exp[-(V_{vapor}/M_{iw}RT^{i}_{H})]\}/$$

$$\{1 - \exp[-(V_{vapor}/M_{iw}RTK^{CH4}_{H})]\})[I]^0. \qquad (6)$$

For both degassing models, if only one inert gas is measured, there is uncertainty in $[CH_4]^0$ because the V_{vapor}/M_{iw} ratio is not determined. However, the magnitude of the uncertainty can be examined by considering the magnitudes of the terms and the limits of equations 3 and 6 as a function of V_{vapor}/M_{iw}. Equations 3 and 6 have the same limits. When $V_{vapor}/M_{iw} >> RTK_H$,

$$[CH_4]^0 = (X_{CH4}/X_I)[I]^0, \qquad (7)$$

and when $V_{vapor}/M_{iw} << RTK_H$, it follows that

$$[CH_4]^0 = (X_{CH4}K^{CH4}_{H}/X_IK^{i}_{H})[I]^0. \qquad (8)$$

That is, if either equilibrium degassing or fractional degassing occurs, $[CH_4]^0$ must have an intermediary value between $(X_{CH4}/X_I)[I]^0$ and $(X_{CH4}K^{CH4}_{H}/X_IK^{i}_{H})[I]^0$. K^{CH4}_{H}/K^{N2}_{H} is ~2 and K^{CH4}_{H}/K^{Ar}_{H} is ~1.5 (Stumm and Morgan, 1981; Pilson, 1998).

Thus, if only the mole fraction of CH_4 and one inert gas are determined, no knowledge of V_{vapor}/M_{iw} creates an uncertainty of ±33% in the calculated mean concentration based on equations 7 and 8 when N_2 is the inert gas and ±20% when Ar is the inert gas.

This limitation can be eliminated, in principle, if an additional inert gas mole fraction or the total pressure is determined. For the case of equilibrium and known total vapor pressure, P_{vapor}, it follows from equation 2 that

$$[CH_4]^0 = [I]^0(X_{CH4}/X_I) + P_{vapor}X_{CH4}(K^{CH4}_{H} - K^{I}_{H}), \qquad (9)$$

and if two inert gases are measured,

$$[CH_4]^0 = ([I_1]^0X_{CH4}/X_{I,1})(\{K^{CH4}_{H} + [([I_1]^0X_{I,2}K^{I,2}_{H} - [I_2]^0X_{I,1}K^{I,1}_{H})/$$

$$([I_2]^0X_{I,1} - [I_1]^0X_{I,2})]\}/\{K^{I,1}_{H} + [([I_1]^0X_{I,2}K^{I,2}_{H} - [I_2]^0X_{I,1}K^{I,1}_{H})/$$

$$([I_2]^0X_{I,1} - [I_1]^0X_{I,2})]\}), \qquad (10)$$

where the sub- and superscript 1 and 2 refer to the two inert gases.

For the case of fractional degassing, $[CH_4]^0$ and $[I]^0$ are given by equation 5. This pair of equations can be solved numerically for $[CH_4]^0$ if P is determined. If two inert gases are measured, P can be eliminated by numerically solving the three equations given by equation 5 for CH_4 and the two inert gases.

We examined the sensitivity of calculated $[CH_4]^0$ on the choice of the model used in the calculation. Calculated $[CH_4]^0$ values as a function of V_{vapor}/M_{iw} for each model were compared. The maximum difference in $[CH_4]^0$ for the two models was found to be small, only 9%, if the reference gas is N_2, and approximately half of this value if Ar is used instead of N_2. This sensitivity results from the fact that the solubility of Ar is more similar to that of CH_4 than is the solubility of N_2.

During sampling of the vapor, it is difficult to avoid contamination with N_2 or Ar from ambient air. However, the extent of contamination can be quantified and subtracted from what is measured based on measured O_2 because methanogenic sediments do not contain any dissolved O_2. The uncertainty because of this correction can also be quantified by conventional methods of propagating errors. The corrected mole fraction, X_I^{corr}, is given by

$$X_I^{corr} = X_I^{meas} - X_{O2}^{meas}\ R, \tag{11}$$

where

X_I^{meas} = the measured mixing ratio of N_2,
X_{O2}^{meas} = the measured mixing ratio O_2, and
R = the atmospheric N_2/inert reference gas molar ratio.

It is important to minimize the amount of contamination because the relative uncertainty of the calculated $[CH_4]^0$ becomes unacceptably large as the mole fraction of inert gas due to contamination approaches X_I^{meas}/R. For example, if it is assumed that all of the relative errors associated with the measurement of CH_4, N_2, or Ar and O_2 are 5%, then in order to keep the uncertainty in the calculated $[CH_4]^0$ below 30%, the measured inert gas/O_2 ratio should be >4.8 for N_2 and 0.073 for Ar (equivalent to ~80% of the inert gas due to contamination).

SAMPLE COLLECTION AND ANALYSIS

All samples analyzed were collected at ODP Site 1230 (D'Hondt, Jørgensen, Miller, et al., 2003), located on the lower slope of the Peru Trench in water of 5086 m depth. This site was the single methane hydrate–bearing site selected for drilling during Leg 201. Sediments of this area are part of the accretionary wedge, located just landward of the Peru Trench (Suess, von Huene, et al., 1988). The upper 200 m of Pleistocene to Holocene sediment is a clay-rich diatomaceous mud. Gas void samples for this study were collected and analyzed from 23 depths between 35 and 170 meters below seafloor (mbsf).

Samples were collected on the ship's catwalk prior to cutting the core into sections. The gas phase was collected directly into a gas-tight syringe fitted with a Luer lock three-way valve. A small hole was drilled into the core liner in the location of a gas void, which allowed a Luer lock tip to fit snugly. The valve and dead space in the syringe were filled with water (preferably helium bubbled or vacuum degassed) to minimize air contamination. The Luer tip was inserted into the hole, and the gas phase was allowed to flush through the side port of the three-way valve. The gas was then directed into the syringe. The gas was allowed to nearly fill the syringe.

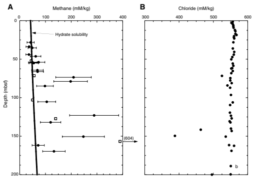
Mole fractions of CH_4, N_2 and O_2 were determined; Ar and total vapor pressure were not measured. The gas was analyzed by gas chromatography with the shipboard natural gas analyzer, which separates these gases on porous polymer and molecular sieve columns in series utilizing thermal conductivity detection. N_2, O_2, and CH_4 were quantified utilizing a standard containing 10% N_2 and 20% CH_4 and air for N_2 and O_2. The assumed value for $[N_2]^0$ used in our calculations, 617 mM/kg, is the equilibrium concentration for salinity 35 and 0°C, the potential temperature of bottom water at Site 1230 (Pilson, 1998).

RESULTS AND DISCUSSION

Calculated $[CH_4]^0$ values (Table **T1;** Fig. **F1**) are given as the mean calculated from equations 7 and 8, $[CH_4]^0_{mean}$, because total pressure and Ar were not measured (see previous sections). The error bars are the limits given by equations 7 and 8 and thus are conservative estimates of the uncertainty. Reproducibility was examined by collecting duplicate samples from two core sections. The average deviation from the mean was 10% for $[CH_4]^0$ based on either the low or high limit. Of the 23 samples collected, 4 were contaminated with air to an extent that resulted in an uncertainty of >30% using an assumed 5% analytical precision for each gas.

T1. In situ CH_4 concentrations, p. 11.

F1. Methane and chloride, p. 10.



The $[CH_4]^0$ values we report, $[CH_4]^0_{mean}$, are the mean values based on equations 7 and 8. $[CH_4]^0_{mean}$ values vary from 36 to 75 mM/kg between 36 and 66 mbsf.

At greater depths, concentrations are more scattered. Much of the scatter at these greater depths is presumably due to the nonuniform distribution of methane hydrate. Chloride concentrations at this site become scattered to lower values at depths >20 mbsf, indicating the presence of methane hydrate that decomposed during core recovery. The additional CH_4 added to the fluid due to hydrate decomposition can be estimated based on the chloride anomaly at a given depth and assuming a H_2O to CH_4 ratio of 5.9 (Davidson, 1983). Between 35 and 66 mbsf, the additional CH_4 due to hydrate decomposition is only ~1–3 mmoles/kg, <13% of the total $[CH_4]^0$. This can be taken as a maximum, as not all of the hydrate decomposed prior to the collection of the vapor phase in the core liner. Below this depth, the greater scatter in the chloride data indicates locally higher abundances of hydrate, indicating potentially large contributions to the measured CH_4.

These results can be compared to the CH_4 concentrations determined using the PCS and to the methane hydrate saturation boundary expected for in situ pressure and temperature. For PCS samples collected in the same depth interval at Site 1230, there is a general agreement with the PCS data (Fig. **F1**) although a detailed comparison is not possible because the samples were not collected from the exact same depth intervals and the nonuniform distribution of hydrate results in scatter (Dickens et al., 2003).

Davie et al. (2004) reported a method for estimating CH_4 solubility with respect to hydrate for seafloor conditions. However, Davie et al. (2004) presented data for pressures up to only 50 MPa, whereas pressures at Site 1230 exceed this number. We have extrapolated their data for use in this study. Based on this extrapolation, and the geotherm at Site 1230, we have plotted the methane hydrate solubility in Figure **F1.** Between 35 and 66 mbsf, the estimated saturation CH_4 concentration varies from ~45 to 49 mM/kg. Our calculated values span this concentration range over this depth interval. Concentrations in excess of those based on solubility can be used to infer the presence of hydrate, and, if the hydrate completely decomposes prior to sampling, its abundance can be quantified.

In summary, in situ dissolved CH_4 concentrations can be determined, with good reproducibility, based on the analysis of exsolved vapor phase CH_4 and N_2 in core liners. Atmospheric contamination can be quantified, and therefore raw data can be quality controlled. Preliminary testing of this method results in values that are consistent with PCS-based measurements and expectations based on methane phase relationships. The method may be further refined and tested, if Ar and/or total pressure are also determined.

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REFERENCES

Claypool, G.E., and Threlkeld, C.N., 1983. Anoxic diagenesis and methane generation in sediments of the Blake Outer Ridge, Deep Sea Drilling Project Site 533, Leg 76. *In* Sheridan, R.E., Gradstein, F.M., et al., *Init. Repts. DSDP,* 76: Washington (U.S. Govt. Printing Office), 391–402.

Clift, R., Grace, J.R., and Weber, M.E., 1978. *Bubbles, Drops, and Particles:* New York (Academic Press).

Davie, M.K., Zatsepina, O.Y., and Buffett, B.A., 2004. Methane solubility in marine hydrate environments. *Mar. Geol.,* 203:177–184. **doi:10.1016/S0025-3227(03)00331-1**

Davidson, D.W., 1983. Gas hydrates as clathrate ices. *In* Cox, J.L. (Ed.), *Natural Gas Hydrates, Properties, Occurrence and Recovery:* Oxford (Butterworth-Heinemann), 1–16.

D'Hondt, S.L., Jørgensen, B.B., Miller, D.J., et al., 2003. *Proc. ODP, Init. Repts.,* 201 [Online]. Available from World Wide Web: **http://www-odp.tamu.edu/publications/201_IR/201ir.htm**

Dickens, G.R., Schroeder, D., Hinrichs, K.-U., and the Leg 201 Scientific Party, 2003. The pressure core sampler (PCS) on ODP Leg 201: general operations and gas release. *In* D'Hondt, S.L., Jørgensen, B.B., Miller, D.J., et al., *Proc. ODP, Init. Repts.,* 201 [Online]. Available from World Wide Web: **http://www-odp.tamu.edu/publications/201_IR/chap_03/chap_03.htm**

Kvenvolden, K.A., and McDonald, T.J., 1986. Organic geochemistry on the *JOIDES Resolution*—an assay. *ODP Tech. Note,* 6.

Martens, C.S., and Berner, R.A., 1974. Methane production in the interstitial waters of sulfate-depleted marine sediments. *Science,* 185:1167–1169.

Pettigrew, T.L., 1992. The design and operation of a wireline pressure core sampler (PCS). *ODP Tech. Note,* 17.

Pilson, M.E.Q., 1998. *An Introduction to the Chemistry of the Sea:* Upper Saddle River (Prentice Hall).

Stumm, W., and Morgan, J.J., 1981. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters* (2nd ed.): New York (Wiley).

Suess, E., von Huene, R., et al., 1988. *Proc. ODP, Init. Repts.,* 112: College Station, TX (Ocean Drilling Program).

APPENDIX

Fractionation during Bubble Growth

The growth rate of a bubble, after nucleation, is predominantly controlled by the mass flux of CH_4 to the bubble. The change in mass within the bubble can be written as

$$(dn_{CH4}/dt) = 4\pi r^2 Q_{CH4}, \tag{A1}$$

where Q_{CH4} is the CH_4 flux to the bubble per unit time. Q_{CH4} depends on the diffusivity of CH_4 in the pore fluid, D^{CH4}, and its solubility, K_H^{CH4}, according to

$$Q_{CH4} = Sh(D^{CH4}/r)K_H^{CH4}[P_w^{CH4} - P_{bub} + P_{H2O} + (2\sigma/4)], \tag{A2}$$

where

Sh = Sherwood number,
$P_w{}^{CH4}$ = t-dissolved CH_4 pressure of the pore fluid prior to ebullition,
P_{H2O} = vapor pressure of water, and
σ = surface tension.

The Sherwood number (Clift et al., 1978) accounts for increased mass flux to the bubble by reduction of the diffusive boundary layer around the bubble in the presence of flow; hence, when Sh = 1, the bubble growth is controlled by diffusion, and Sh > 1 can be assumed if the fluid is mixing during the ebullition process, as we expect. A characteristic timescale for the growth of a bubble of maximum radius, r_{max}, just before leaving the sediment into the headspace is, then,

$$\tau_{growth} = (n/4\pi r^2 Q_{CH4}) =$$

$$(P_{bub}r_{max}{}^2/\{3RTShD^{CH4}K_H^{CH4}[P_w^{CH4} - P_{bub} + P_{H2O} + (2\sigma/r_{max})]\}). \tag{A3}$$

Because CH_4 controls the total pressure of the bubble, the bubble will scavenge trace gases (like N_2 and Ar) as it grows in a characteristic time scale:

$$\tau_{trace} = (n/4\pi r^2 Q_{trace}) = (r^2/3RTShD^{trace}K_H^{trace}). \tag{A4}$$

As the bubble grows, it will accumulate more quickly the more soluble and more diffusive trace gases from the pore fluid. The scavenging efficiency will depend on K_H^{N2}/K_H^{CH4} (or K_H^{Ar}/K_H^{CH4}) or, and to a lesser extent, on D^{N2}/D^{CH4} (or D^{Ar}/D^{CH4}) because for N_2, Ar, and CH_4, the greatest differences are in their solubility coefficients. As the ebullition process continues, the concentration of the trace gases in the pore fluid will decrease with time according to the ratio of $\tau_{growth}/\tau_{trace}$. Clearly, the headspace will initially accumulate the more soluble and more diffusive trace gases early on in the ebullition process.

Figure F1. **A.** Methane concentrations for Site 1230 derived from gas void analyses. Circles = mean of calculated concentrations based on equations 7 and 8. Error bars cover the range of the values. Squares = concentrations derived from PCS measurements (Dickens et al., 2003) calculated following Milkov et al., (2003). **B.** Chloride vs. depth for Site 1230 (D'Hondt, Jørgensen, Miller, et al., 2003).

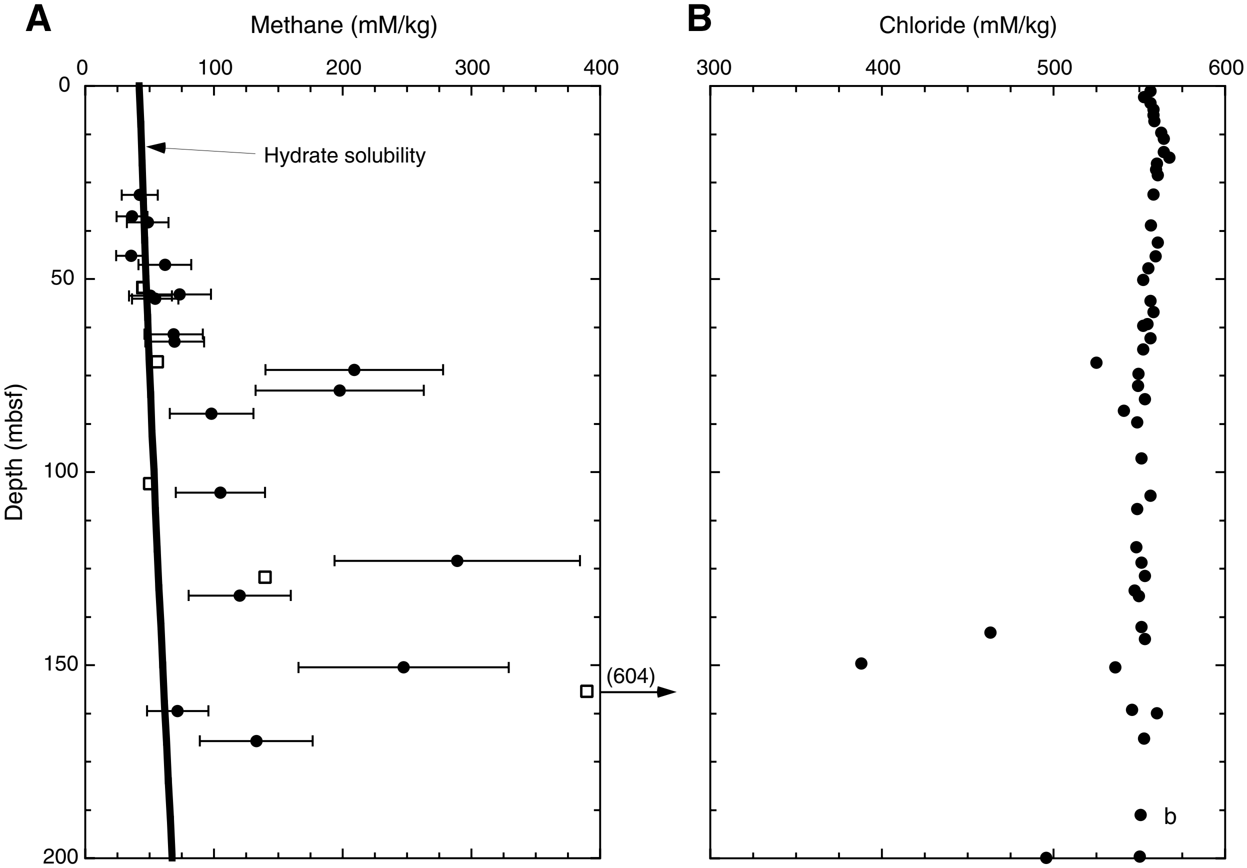

Table T1. In situ CH_4 concentrations, Site 1230.

Core, section	Depth (mbsf)	N_2/O_2	CH_4/N_2	CH_4 (mmol/kg)
201-1230A-				
4H-6	28.3	5.2	13.4	42.6
5H-1	33.8	16.1	30.3	36.5
6H-3	46.3	9.6	41	62.1
7H-3	54.0	7.8	41.5	73.5
9H-4	64.3	13.5	53.8	68.8
10H-3	73.6	5.1	62.7	209
11H-6	85.0	3.7	0.6	Contaminated
12H-1	90.4	3.8	6.5	Contaminated
13H-5	105.3	5.4	35.2	105
14H-6	116.4	3.7	0.5	Contaminated
15H-5	123.0	6.8	140	289
17H-1	132.0	6.4	54.1	120
19H-2	150.6	5.7	93.5	248
21H-4	161.9	9.1	46.1	72
22H-2	169.7	11.3	96.3	133
201-1230B-				
12H-3	84.9	13.2	76.3	98.2
11H-5	78.9	17.3	168	198
7H-6	50.1	3.7	0.2	Contaminated
8H-2	55.2	10.2	37.5	54.5
9H-1	66.3	12.4	52.7	69.6
8H-2	54.4	13.2	39.5	50.8
7H-1	44.0	25.7	33.1	35.9
6H-1	35.4	11.3	35.3	48.7

Notes: Concentrations are based on the mean values calculated using equations 7 and 8 (see text). As described in the text, uncertainty due to not knowing V_{vapor}/M_{iw} is ±33% from the calculated mean. Samples are identified as contaminated if they are contaminated to an extent that creates an uncertainty >33%.