

6. GAS HYDRATE ESTIMATES FROM NEWLY DETERMINED OXYGEN ISOTOPIC FRACTIONATION ($\alpha_{\text{GH-IW}}$) AND $\delta^{18}\text{O}$ ANOMALIES OF THE INTERSTITIAL WATERS: LEG 164, BLAKE RIDGE¹

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ABSTRACT

The $\delta^{18}\text{O}$ values of interstitial waters from Site 994 and Site 997 sediments, Blake Ridge, western Atlantic, tend to decrease with depth from 0.3‰ to -0.5‰ Standard Mean Ocean Water in the upper 200 mbsf, then fluctuate with significant positive spikes of $\Delta = 0.2\text{‰}$ –0.5‰ in the gas hydrate zone (200 to 450 mbsf), and finally increase from -0.4‰ to -0.2‰ toward 700 mbsf. Positive shifts of $\delta^{18}\text{O}_{\text{IW}}$ in the gas hydrate zone are probably caused by the dissociation of gas hydrates originally contained in sediment cores. Gas hydrates recovered from the sites are enriched in ^{18}O , $\delta^{18}\text{O}$ ranging between 2.7‰ and 3.5‰. $\delta^{18}\text{O}$ values of gas hydrates and ambient interstitial waters give an oxygen isotopic fractionation factor of 1.0034–1.0040 at 12°C–16°C and ~31 MPa (3 km below sea level). Based on this fractionation and observed isotopic anomalies in the gas hydrate zone, gas hydrates occupy 6% to 12% of pore-space volume within Blake Ridge sediments.

INTRODUCTION

Interest in marine gas hydrates has grown as earth science researchers look at the potential influence of gas hydrates on global climatic change, long-term energy resources, and natural hazards such as slope instability and submarine methane expulsion. The most critical and fundamental question in gas hydrate study is: how much gas hydrate is stored in marine sediments? Variable estimates have been reported (e.g., McIver, 1981; Kvenvolden, 1988; Dillon et al., 1995), but global inventory of gas hydrate is believed to be 10^4 Gt (10^{19} g) as carbon (Kvenvolden, 1988). This large estimate has highlighted the potential importance of marine gas hydrates, but the global inventory of gas hydrate requires further refinement through the assessment of local marine gas hydrate amounts.

Assessment of gas hydrate amounts in hydrate-bearing sediments has been made using various techniques such as seismic investigations, well logging, geochemical investigations, and temperature measurements. Chloride anomalies in interstitial water are believed to be a reliable method of estimating gas hydrate amounts, as documented during Ocean Drilling Program (ODP) Leg 164 (Paull, Matsumoto, Wallace, et al., 1996). Recently, however, a serious question has been raised concerning the effects of selective filtration/adsorption on some chemical elements during mechanical squeezing (Cave et al., 1998). This problem seems to require reassessment of the chloride anomaly technique.

The water within gas hydrate is enriched in isotopically heavy oxygen (^{18}O) relative to ambient waters (e.g., Hesse and Harrison, 1981; Harrison and Curiale, 1982; Ussler and Paull, 1995). Consequently, gas hydrate should be an enormous sink of ^{18}O in the earth's surface, analogous to polar ice. Matsumoto and Matsuda (1987) and Matsumoto (1989) have argued for a genetic relationship between heavy-oxygen-containing siderites and in situ dissociation of gas hydrates, and have suggested that diagenetic carbonates would provide a unique tool to identify fossil gas hydrate horizons in ancient sedimen-

tary rock sequences. Interstitial waters squeezed from gas hydrate-bearing sediments are expected to be variably enriched in ^{18}O , depending on the amount of gas hydrate present, hence, deviations in $\delta^{18}\text{O}$ of pore waters from baseline values (the $\delta^{18}\text{O}$ anomaly) should be an independent technique in estimating gas hydrate amount. However, the isotopic fractionation factor for oxygen has not been determined yet for any clathrate system, except for the experimental study on the THF (tetrahydrofuran) hydrate and water (Davidson et al., 1983).

Leg 164 coring recovered several massive gas hydrate samples and collected hundreds of interstitial water samples from Blake Ridge sediments, offering a unique opportunity to estimate the oxygen isotopic fractionation factor ($\alpha_{\text{GH-IW}}$) for naturally occurring methane gas hydrate. In this study, we measured $\delta^{18}\text{O}$ of gas hydrates and ambient interstitial waters to determine $\alpha_{\text{GH-IW}}$. We then estimated the gas hydrate amount in Blake Ridge sediments on the basis of observed $\delta^{18}\text{O}$ anomalies and compared the results with those of the chloride anomaly technique.

SAMPLES AND EXPERIMENTAL METHODS

Gas Hydrates

A number of massive gas hydrate samples were recovered from Sites 994 and 997 on the Blake Ridge and from Site 996, an active vent site on the Blake Ridge Diapir (Fig. 1). Methane gas hydrates recovered from the Blake Ridge were ice-like, translucent white solids a few centimeters in diameter and more than 35 cm in length, whereas those from the Blake Ridge Diapir were friable vein-fillings, measuring a few millimeters thick, with near-vertical orientation (Paull, Matsumoto, Wallace, et al., 1996). After 5 to 10 min of observation and photographing on the catwalk, solid gas hydrates were hand-picked or cut from the sediment cores, transferred to pressure vessels, and stored in a freezer at -20°C. The pressure vessels were shipped to Tokyo by air cargo from Miami and arrived in Tokyo within 36 hours after the end of the cruise.

One gas hydrate sample from Site 994 and three samples from Site 997 were analyzed for $\delta^{18}\text{O}$. These samples were well preserved, whereas vein-filling gas hydrate from Site 996 were apparently contaminated with pore waters and so were of no use. We interpret that gas hydrates from Site 996 dissociated within the pressure vessels during transport and storage.

¹Paull, C.K., Matsumoto, R., Wallace, P.J., and Dillon, W.P. (Eds.), 2000. *Proc. ODP, Sci. Results*, 164: College Station, TX (Ocean Drilling Program).

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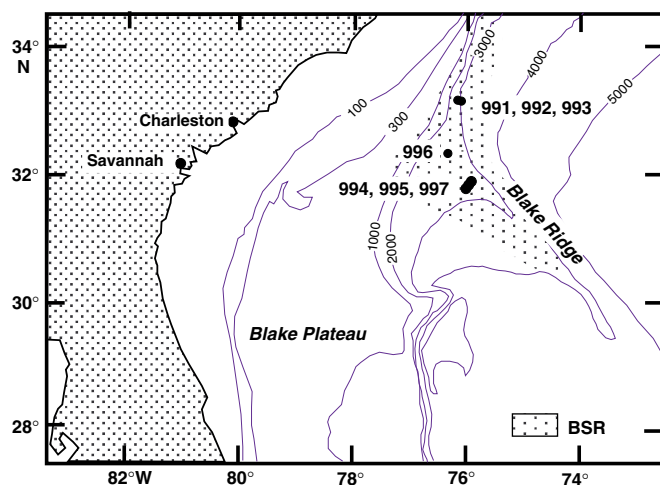


Figure 1. Map showing the locations of drilling sites of Leg 164. Bathymetric contours in meters.

Sample 2A

Sample 2A, ~30 cm³ in volume, was selected from one of five large pieces of white, irregularly shaped nodules with soapy luster that were embedded in nanofossil-rich clay (Sample 164-994C-31X-7, 10–50 cm; 259.90–260.30 mbsf). The broken appearance of the hydrate and the disturbance of the host sediments suggest that the recovered samples were originally present as layers that were broken during coring and recovery. Occurrence of massive gas hydrate from this horizon seems to correspond to the zone of anomalously high electrical resistivity of the interval between 220 and 260 mbsf (Paull, Matsumoto, Wallace, et al., 1996).

Samples 14, 16A, 16B, 16C

Several large pieces of massive gas hydrate were recovered from Hole 997A (Sample 164-997A-42X-3, 0–55 cm (330.03–330.58 mbsf)). The top 20 cm of the sample contained 10 to 15 angular fragments of white, fizzing hydrate, 3–10 cm in diameter, in nanofossil-rich clay that was disturbed by drilling. The next 27-cm section consists of a single piece of solid gas hydrate, which was broken into three pieces, 5, 7, and 15 cm long. Sample 14 was taken from the top 20 cm of the section (Sample 164-997A-42X-3, 0–20 cm; 330.03–330.23 mbsf), and samples 16A and 16B (Sample 164-997A-42X-3, 20–25 cm; 330.23–330.48 mbsf) and 16C (Sample 164-997A-42X-3, 25–32 cm; 330.48–330.55 mbsf) were taken from the top two pieces of the continuous gas hydrate section. The surface of these continuous gas hydrate samples was coated by thin (<1 mm), transparent shiny layer of water ice. The sediments immediately below the continuous hydrate sample contained small rectangular fragments of gas hydrate in slightly soupy, disturbed clay. Well logging conducted in Hole 997B, 25 m northwest of Hole 997A, observed anomalously high resistivity at 360–365 mbsf, 30–35 m deeper than thick massive gas hydrate horizon in Hole 997A (Paull, Matsumoto, Wallace, et al., 1996). If the high-resistivity zone corresponds to massive gas hydrate, this may suggest that the thick occurrence is not bedded, but perhaps fills an inclined fault.

Interstitial Waters

Interstitial waters were extracted from whole-round sections of sediments, 10 to 25 cm long, using a Manheim hydraulic squeezer. These water samples were stored in flame-sealed glass ampoules immediately after extraction. Thirteen samples from Site 994 (57.85 to 686.53 mbsf) and 21 samples from Site 997 (5.80 to 746.85 mbsf) were selected for isotopic analysis of pore-water oxygen ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$).

Experimental Procedures

Each gas-hydrate sample was placed in a teflon-coated dissociation chamber to decompose at room temperature. Gas pressure within the chamber steadily increased and reached stability in about 10 min, then the gas was transferred to a small collection chamber for further analysis. The measurements include gas composition and carbon and hydrogen isotopic composition (the results are given in Matsumoto et al., Chap. 2, this volume). The volume of the residual water was measured and stored in flame-sealed glass tubes for isotopic analysis. Chloride concentration was also measured to estimate the amount of pore water that mixed with water derived from gas hydrate.

The standard CO₂-equilibrium method of Epstein and Mayeda (1953), as modified by Matsuhisa and Matsumoto (1986), was used to measure the oxygen-isotopic composition of gas hydrate and interstitial water. Water aliquots (1.0–1.5 mL; 28 to 42 mmol O₂) were sealed in a small flask with 0.10 mmol of CO₂ of known isotopic composition. The flasks were placed in a water bath (25.0°C) and stirred for 15–20 hr so that oxygen-isotopic equilibrium occurred between the water and CO₂ phases. After complete isotopic exchange, the CO₂ gas was removed and refined within a cryogenic vacuum line. The oxygen isotopic ratio ($^{18}\text{O}/^{16}\text{O}$) of the equilibrated CO₂ gas was determined using Finnigan Delta E and Delta S mass spectrometers. The results are represented in per-mil delta notation ($\delta^{18}\text{O}$, ‰) relative to Standard Mean Ocean Water (SMOW). The standard deviation (2 σ) of independent analyses was 0.01‰–0.05‰, whereas the reproducibility of the measurements was ~0.10‰ as estimated from the duplicate analysis of CO₂ gas samples that were prepared from the identical water sample.

Chloride concentration of gas hydrate-derived waters were measured using an ion chromatograph (ICA-5000). Standard deviation of the measurements is ~2%.

RESULTS AND DISCUSSION

Interstitial Waters

Site 994

The $\delta^{18}\text{O}$ values of the interstitial waters from Site 994 show a fairly smooth variation with depth with values ranging from 0.30‰ to –0.37‰ (Table 1, Fig. 2A). The $\delta^{18}\text{O}$ profiles show consistent characteristics within three depth zones: an upper (top 250 mbsf), a middle (250–500 mbsf), and a lower unit (500–700 mbsf). The middle unit roughly corresponds to the gas hydrate zone (Paull, Matsumoto, Wallace, et al., 1996). In the upper unit, $\delta^{18}\text{O}$ values decrease with depth from ~0.3‰ to –0.4‰, whereas values of the lower unit increase slightly from –0.2‰ to reach between 0‰ and 0.2‰. In the middle unit, $\delta^{18}\text{O}$ values increase with depth, showing a sharp drop at 456.25–485.93 mbsf, which coincides with the bottom-simulating reflector (BSR). The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values from samples within the gas hydrate zone represent mixing of water derived from dissociated gas hydrate and from pristine *in situ* pore water. To evaluate the meaning of the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ data, one must be able to separate these signals, so we have constructed a regression curve representing the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of the *in situ* pore water only (dotted curve, $r^2 = 0.9905$, Figure 2A). This curve is based on best-fit polynomial function using only data above (2 data points) and below (6 data points) the gas hydrate zone. Apparent positive shifts in $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ from the baseline may be related to the existence of gas hydrate in these sediments, as gas hydrate should yield ^{18}O -enriched water to the pore waters.

Site 997

The $\delta^{18}\text{O}$ of the interstitial water samples from Site 997 range from 0.25‰ (5.8 mbsf) to –0.54‰ (347.95 mbsf) (Fig. 2B). The overall trend is similar to that of Site 994, decreasing in the top 200 m and increasing in the lower unit below ~500 mbsf. The regression

Table 1. Oxygen isotopic composition of the interstitial waters from Sites 994 and 997.

Core, section, interval (cm)	Depth (mbsf)	$\delta^{18}\text{O-H}_2\text{O}$ (‰ SMOW)
164-994C-		
7H-4, 145-150	57.85	0.32
15H-5, 142-147	126.18	-0.09
164-994D-		
3X-1, 140-150	252.80	-0.37
164-994C-		
41X-3, 122-132	341.67	-0.17
164-994D-		
8X-3, 135-150	400.15	-0.13
164-994C-		
52X-2, 137-147	427.37	-0.06
164-994C-		
56X-2, 135-150	456.25	-0.02
59X-3, 135-150	485.93	-0.15
63X-4, 135-150	516.03	-0.04
67X-4, 118-128	546.63	0.02
72X-1, 135-150	579.85	0.03
79X-6, 118-133	653.10	0.15
83X-2, 135-150	686.53	0.08
164-997A-		
2H-2, 140-150	5.80	0.25
2H-5, 140-150	10.30	0.27
4H-1, 140-150	23.30	0.19
4H-6, 140-150	30.80	0.15
10H-6, 140-150	79.65	0.11
15H-2, 140-150	125.80	-0.10
20H-1, 135-150	158.75	-0.24
28X-1, 130-150	222.90	-0.35
31X-1, 130-150	242.20	-0.31
31X-4, 130-150	246.70	-0.19
32X-3, 130-150	254.80	-0.22
32X-4, 70-90	255.70	-0.08
41X-4, 130-150	324.50	-0.27
42X-2, 88-113	329.78	-0.37
164-997B-		
3X-3, 125-150	341.67	-0.17
164-997A-		
44X-1, 125-150	347.95	-0.54
46X-5, 125-150	372.90	-0.25
164-997B-		
8X-6, 125-150	451.65	0.22
19X-2, 125-150	532.35	-0.20
38X-2, 125-150	676.55	0.16
47X-4, 125-150	746.85	-0.01

for the $\delta^{18}\text{O}$ values of the pristine pore water was constructed based on 7 data points above and 3 data points below the gas hydrate zone ($r^2 = 0.9890$, Fig. 2B). The curve indicates that the pristine pore waters of gas hydrate zone are significantly depleted in ^{18}O . Values from samples of the gas hydrate zone are highly variable, and the positive excursions are much larger relative to those of Site 994. The magnitude of positive shifts in gas hydrate zone is 0.3‰–0.6‰, almost twice as large as those of Site 994.

Oxygen Isotopic Anomalies vs. Chloride Anomalies

The dilution of pore waters by freshwater derived from dissociating gas hydrate decreases the chloride concentration in recovered interstitial waters. The difference between measured chloride concentration in recovered samples and that of calculated, in situ values is the chloride anomaly of gas hydrate–zone samples (Paull, Matsu-moto, Wallace, et al., 1996). The $\delta^{18}\text{O}$ anomalies are defined as the difference between $\delta^{18}\text{O}$ of recovered interstitial waters and $\delta^{18}\text{O}$ of pristine in situ pore waters, which is given by the polynomial fits of the respective sites (Fig. 2A, B). If the gas hydrate dissociation is also responsible for the deviation from the baseline $\delta^{18}\text{O}$ values by adding ^{18}O to pore waters, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ anomalies should be correlative with chloride anomalies. To test this possible correlation, both anomalies are shown in Figure 3. The occurrence and magnitude of chloride and $\delta^{18}\text{O}$ anomalies are generally correlative. For example, the largest measured $\delta^{18}\text{O}$ anomaly (451.64 mbsf) is directly correlative with a large chloride anomaly. The covariation between chloride and $\delta^{18}\text{O}$

anomalies is also shown in Figure 4, where a least-squares linear regression gives a correlation coefficient (r^2) of 0.76.

Gas Hydrates

Results of $\delta^{18}\text{O}$ measurements of water derived from gas hydrate samples are given in Table 2 along with gas and water volumes, and chloride concentrations. These $\delta^{18}\text{O}$ values were corrected for mixing with interstitial water, probably coming from sediment adhering to the gas hydrate samples. Gas hydrates are assumed to contain only freshwater (e.g., Hesse and Harrison, 1981), whereas interstitial waters are assumed to have a baseline value of chloride (Paull, Matsu-moto, Wallace, et al., 1996).

Chloride concentrations of the interstitial waters are given in Figure 5. Chloride concentrations within the interval 200–450 mbsf (gas hydrate zone) are highly irregular, with sharp spikes toward lower concentration values. These chloride fluctuations are interpreted to represent differing amounts of gas hydrate contained within the sediment samples, which contribute freshwater to sediment pore waters as they dissociate during core recovery and processing. Paull, Matsu-moto, Wallace, et al. (1996) calculated the in situ chloride concentration through the gas hydrate zone using a polynomial best fit to chloride concentration data above and below the gas hydrate-containing zone (dashed line in Figure 5). Baseline chloride concentration values are 505 mM and 509 mM for Site 994 and 997, respectively.

Because gas hydrate should be composed of freshwater, chloride values above 0 mM represent introduction of pore water of varying amounts into the gas hydrate water. Chloride concentrations of five water samples derived from gas hydrate are 5 to 62 mM (Table 2). Using the in situ chloride concentration values listed above, the mole fraction of gas hydrate water in water samples is 0.990–0.878. Correcting for pore water contamination, $\delta^{18}\text{O}$ values of gas hydrate water is 2.67‰ for Section 164-994C-31X-7 and 2.82–3.51‰ (mean = 3.2‰) for Section 164-997A-42X-3. Note that the isotopic value for Site 997 samples differs by about 20%.

Oxygen Isotopic Fractionation Between Gas Hydrate and Ambient Water

The $\delta^{18}\text{O}$ of interstitial waters and gas hydrates at Sites 994 and 997 are collectively shown in Figure 6. The difference in $\delta^{18}\text{O}$ values between gas hydrate and the ambient water ($\Delta\delta^{18}\text{O}_{\text{GH-IW}}$) is 3.1‰ at Site 994 and 3.3–3.8‰ (mean = 3.6‰) at Site 997. Given that recovered massive gas hydrates were in isotopic equilibrium with ambient interstitial waters ($T = 12^\circ\text{--}16^\circ\text{C}$ and $P = 31\text{ MPa}$), the equilibrium isotopic fractionation factor ($\alpha_{\text{GH-IW}}$) at each site is 1.0034 (Site 994) and 1.0037–1.0040 (Site 997). For comparison, the oxygen-isotopic fractionation of ice–water is 1.0027–1.0035 (O’ Neil, 1968; Craig and Hom, 1968; Jakli and Staschewski, 1977) and that of the THF hydrate–water association is 1.00268 ± 0.00003 at $0^\circ\text{--}4^\circ\text{C}$ (Davidson et al., 1983).

The gas hydrate occurrence depth does not necessarily indicate that gas hydrate formed at that depth. The hydrate may have been formed at a shallower depth and subsequently buried deeper within the sediment column. Thus, recovered gas hydrates are not necessarily in isotopic equilibrium with the ambient pore waters. A wide range in $\delta^{18}\text{O}$ values for Site 997 gas hydrate seems to suggest that the gas hydrate formed over a long time and incorporated water from temporally and spatially changing pore waters. Alternatively, the massive gas hydrate at Site 997 may have formed in fractures associated with upward-migrating water enriched in ^{18}O .

Gas Hydrate Amounts

As mentioned above, $\delta^{18}\text{O}$ anomalies of interstitial waters of the gas hydrate zone are explained as the results of mixing of pristine pore water with isotopically heavy water released by the dissociation of gas hydrate. Assuming that the Blake Ridge gas hydrate has a stoi-

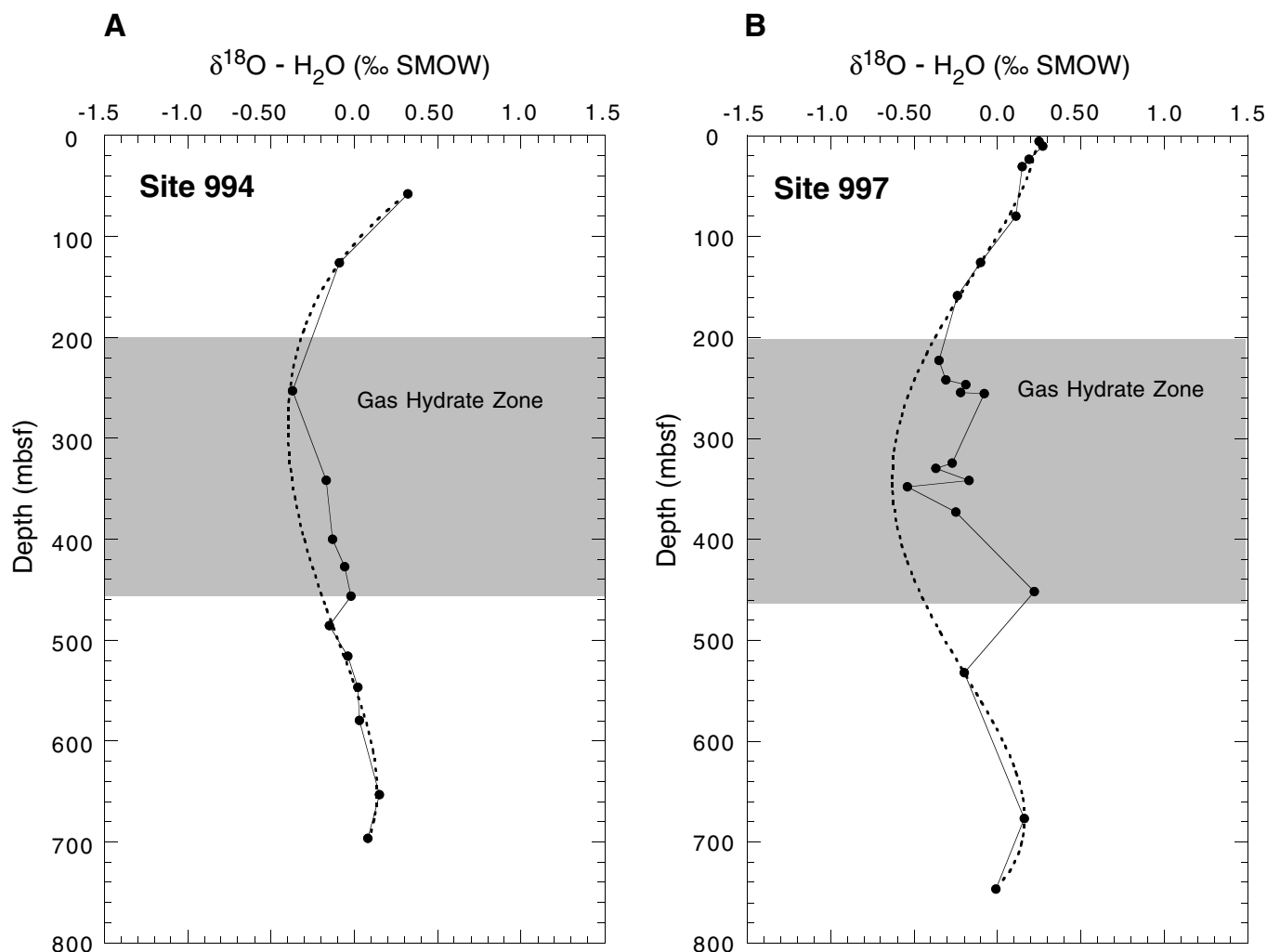


Figure 2. The $\delta^{18}\text{O}$ (‰ SMOW) of interstitial waters at (A) Site 994 and (B) Site 997. Dotted lines represent baselines for the interstitial waters seemingly unaffected by gas hydrate dissociation. Baseline for Site 994: $Y = 0.886 + (-1.20\text{e-}02)X + (4.23\text{e-}05)X^2 + (-8.06\text{e-}08)X^3 + (1.01\text{e-}10)X^4 + (-5.85\text{e-}14)X^5$, ($r^2 = 0.9906$). For Site 997: $Y = 0.245 + (-7.43\text{e-}04)X + (-2.44\text{e-}05)X^2 + (7.29\text{e-}08)X^3 + (-4.82\text{e-}11)X^4 + (-6.34\text{e-}5)X^5$, ($r^2 = 0.9890$), where Y is $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰ SMOW) and X is depth (mbsf).

chiometric composition ($\text{CH}_4 \cdot 5.75 \text{H}_2\text{O}$; $M = 16.0 + 103.5 = 119.5$ g) and the density of methane hydrate is 0.91 g/cm^3 (MacDonald, 1990; Makogon, 1997), the volume ratio of gas hydrate water to gas hydrate is $103.5 : 119.5/0.91 = 0.79 : 1$. Using the gas hydrate–water fractionation ($\Delta\delta^{18}\text{O}_{\text{GH-IW}}$) value of 3.1‰ at Site 994 and 3.6‰ at Site 997, which were derived above, the relationship between the measured $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values ($\delta^{18}\text{O}_M$) and the pristine pore water ($\delta^{18}\text{O}_P$) at Site 994 is expressed as:

$$(1 - 0.21X) \delta^{18}\text{O}_M = 0.79 X (\delta^{18}\text{O}_P + 3.1) + (1 - X) \delta^{18}\text{O}_P \quad (1)$$

where X is the pore saturation of gas hydrate, that is, the fraction of pore space occupied by gas hydrate, and $(1 - 0.21X)$, $0.79X$, and $(1 - X)$ are mole fraction of mixed water, gas hydrate water, and pristine pore water, respectively. Solving Equation 1 for X gives:

$$X = (\delta^{18}\text{O}_M - \delta^{18}\text{O}_P) / [2.4 + 0.21 (\delta^{18}\text{O}_M - \delta^{18}\text{O}_P)]. \quad (2)$$

For Site 997, Equation (2) should be,

$$X = (\delta^{18}\text{O}_M - \delta^{18}\text{O}_P) / [2.8 + 0.21 (\delta^{18}\text{O}_M - \delta^{18}\text{O}_P)]. \quad (3)$$

Gas hydrate amounts (pore saturation%) in sediments are calculated and given in Figure 7 along with gas hydrate estimates from chloride anomalies (Paull, Matsumoto, Wallace, et al., 1996).

At Site 994, five samples in the gas hydrate zone yield a gas hydrate saturation of 6.2% , which is almost twice as much as the estimates based on chloride anomalies (Paull, Matsumoto, Wallace, et al., 1996). At Site 997, the gas hydrate amount shows a rapid increase to 16% in the interval $230\text{--}340$ mbsf in the gas hydrate zone, and a sharp drop at 348 mbsf, before reaching a maximum value of 25% at 451 mbsf just above the BSR depth. The average amount of gas hydrate is around 12% , which is also about two times greater than the amount based on chloride anomalies.

The observed discrepancy between the two estimates is not great but not insignificant. The possible causes of the discrepancy are (1) uncertainty in the determination of baselines (in situ trends) of both $\delta^{18}\text{O}$ and chloride concentration, (2) differential chemical effects between ^{18}O and Cl^- during mechanical squeezing (Cave et al., 1998), and (3) sample deterioration, which may have occurred during storage of water samples. The baseline factor is thought to be most critical, because its calculation may involve large uncertainties. Also, the sampling density may partially explain the apparent discrepancy. Samples for chloride analyses were more densely spaced than those

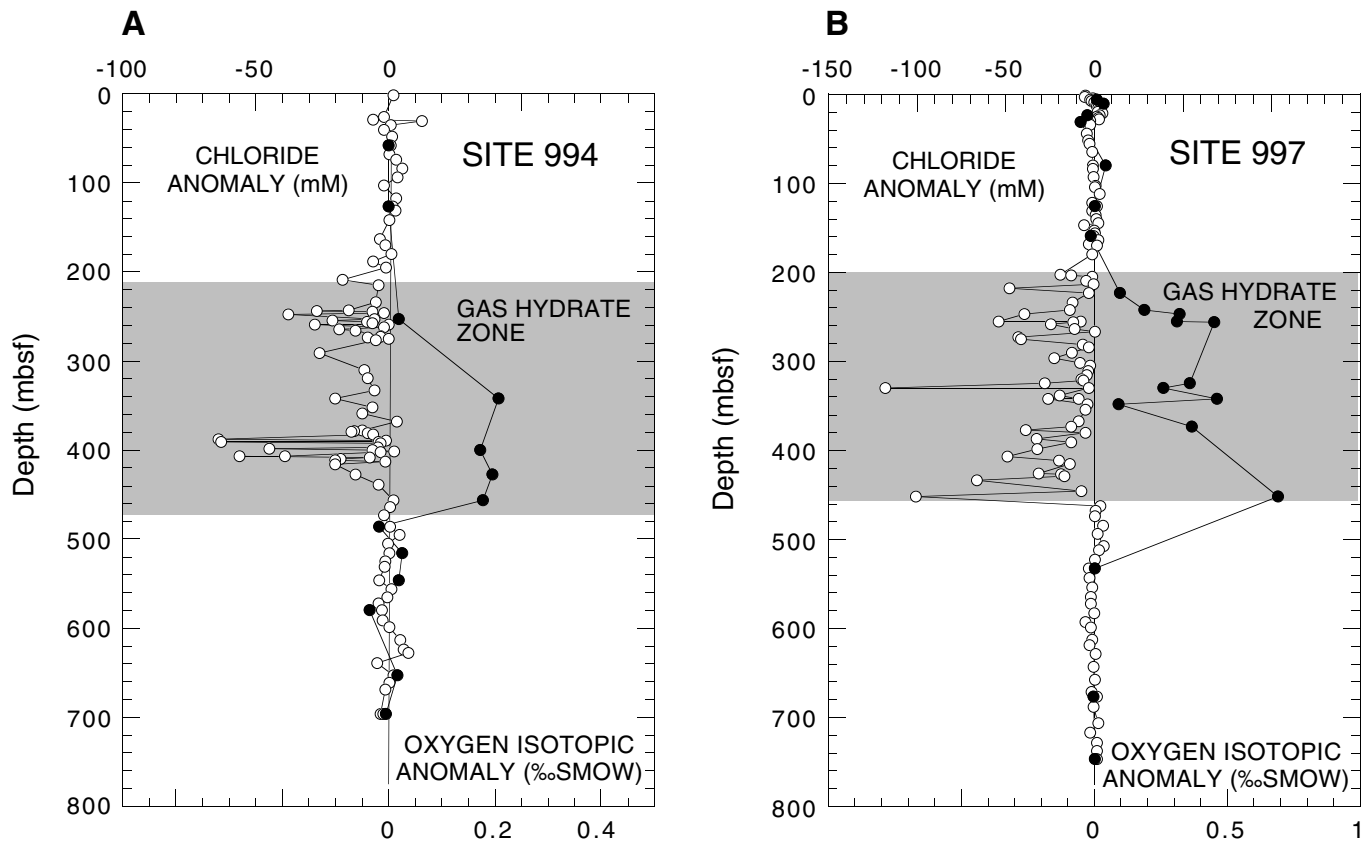


Figure 3. Correlation between $\delta^{18}\text{O}$ anomaly (solid circles) and chloride anomaly (open circles) of the interstitial waters at (A) Site 994 and (B) Site 997.

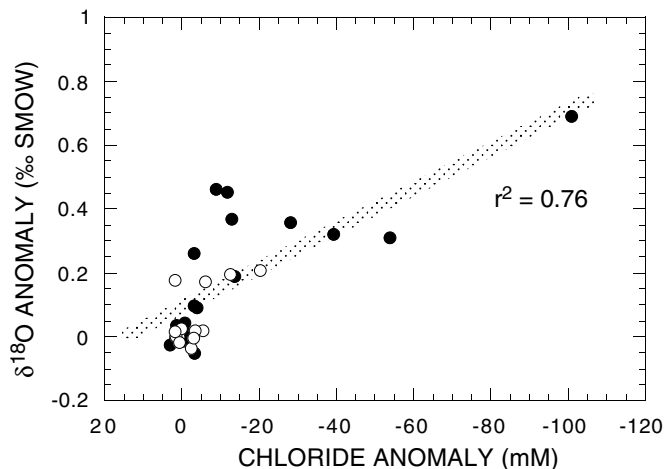


Figure 4. Crossplot of $\delta^{18}\text{O}$ anomaly vs. chloride anomaly of Site 994 (open circles) and Site 997 (solid circles). Regression coefficient (r^2) = 0.76.

for isotope analyses, plus they were taken in gas hydrate-free sediments, whereas sparsely spaced $\delta^{18}\text{O}$ samples were obtained mainly from hydrate occurrences and therefore did not unambiguously detect hydrate-free horizons within the gas hydrate zone.

Determining the amount of methane gas hydrate stored in marine sediments is of paramount importance. Assessing the environmental impact of marine gas hydrates is wholly dependent on knowing gas hydrate amounts and occurrence. Moreover, any assessment of the resource potential of gas hydrates is impossible without knowing the amount of gas hydrates in the target areas. Several alternative

approaches toward gas hydrate estimates include geophysical surveys, well logging, and sediment temperature measurements, but the geochemical approach is likely to give the most reliable quantitative estimates presently. These geochemical methods are dependent on the chemical composition of pore waters unaffected by sampling and recovery; therefore, it is crucial to develop new technologies to recover in situ pore waters from gas hydrate-bearing sediments. In this way, local estimates of gas hydrate amounts may be refined, and the global inventory of marine gas hydrate can be incrementally improved.

CONCLUSIONS

1. The $\delta^{18}\text{O}$ of the interstitial waters of the Blake Ridge sediments tends to decrease with depth from +0.5‰ SMOW of the bottom seawater value to about -0.5‰ at around 300 mbsf, then recover to +0.2‰ at ~700 mbsf.

2. Interstitial waters squeezed from gas hydrate-bearing sediments are significantly and variably enriched in ^{18}O , reflecting the donation of ^{18}O -enriched water derived from dissociated gas hydrate to pore waters.

3. The $\delta^{18}\text{O}$ anomalies within the gas hydrate zone correlate with chloride anomalies.

4. Calculated equilibrium fractionation factors (α) between natural gas hydrates and interstitial waters are 1.0034 at Site 994 and 1.0037–1.0040 at Site 997.

5. The $\delta^{18}\text{O}$ anomalies within the gas hydrate zone indicate mean values of about 6% (pore saturation) at Site 994 and 12% at Site 997, which are about twice as much as those estimated from chloride anomalies.

Table 2. Oxygen isotopic composition (‰ SMOW) of gas hydrate waters from Sites 994 and 997.

Core, section	Laboratory sample no.	Depth (mbsf)	Measured $\delta^{18}\text{O}$ of H_2O (‰ SMOW)	$[\text{Cl}^-]$ of H_2O (mM)	$[\text{Cl}^-]$ of pristine pore water (mM)	$\delta^{18}\text{O}$ of pristine pore water (‰ SMOW)	Mole fraction of gas hydrate water	$\delta^{18}\text{O}$ of gas hydrate water (‰ SMOW)
164-994C-31X-7	2A	259.90	2.6	17	505	-0.4	0.966	2.7
164-997A-42X-3	14	330.15	2.7	20	509	-0.5	0.961	2.8
42X-3	16A	330.25	3.3	5	509	-0.5	0.990	3.3
42X-3	16B	330.25	3.2	41	509	-0.5	0.919	3.5
42X-3	16C	330.30	2.7	62	509	-0.5	0.878	3.2

Note: Measured $\delta^{18}\text{O}$ values were corrected for contamination by the pristine pore water using the baseline values of chloride concentration (Cl^- mM; Fig. 5) and $\delta^{18}\text{O}$ values (Fig. 2).

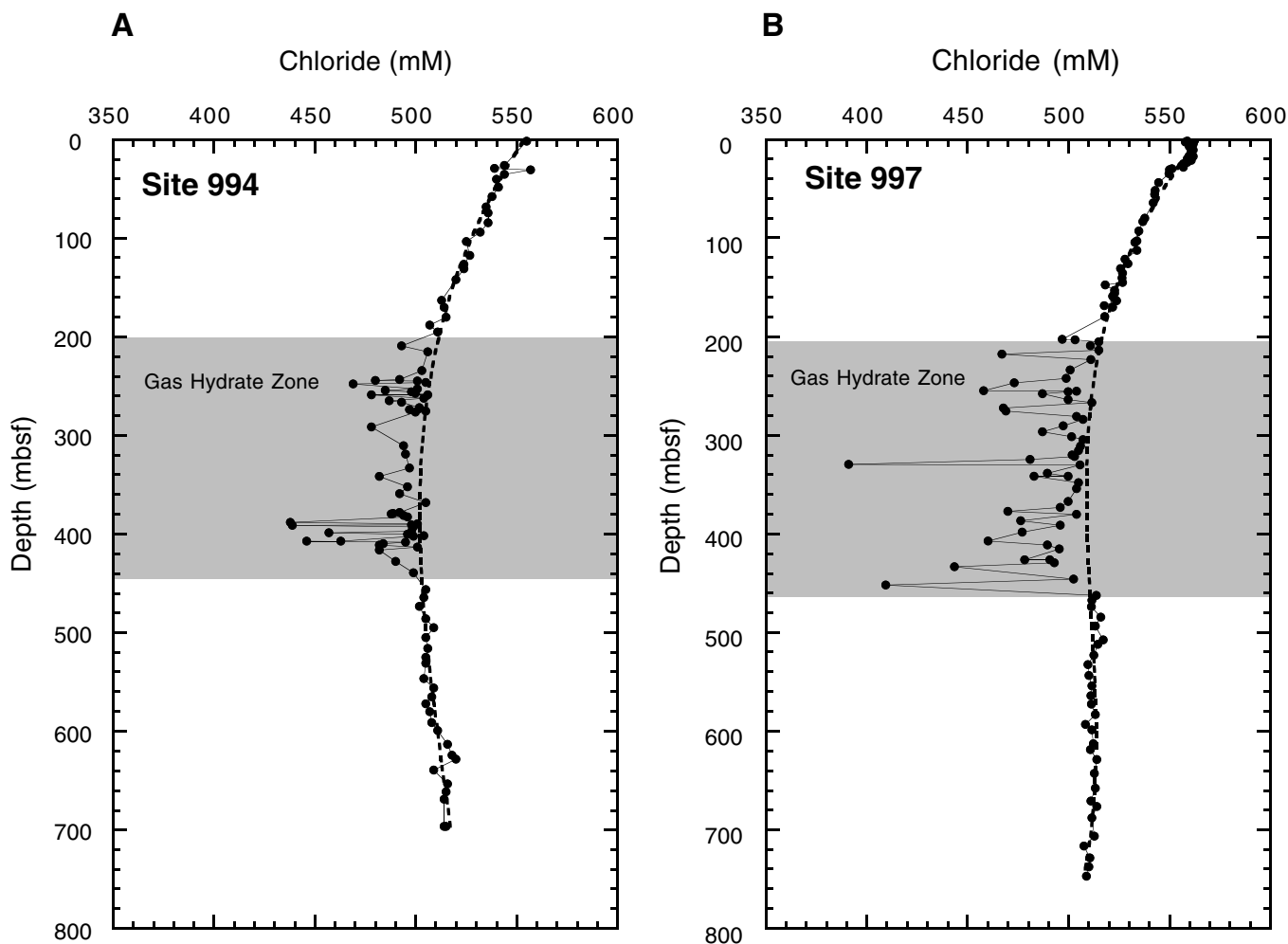


Figure 5. Depth profiles of chloride concentration of the interstitial waters from (A) Site 994 and (B) Site 997. Baselines for pristine interstitial waters unaffected by gas hydrate dissociation are shown by dashed lines. Gas hydrate-bearing zones are shown by shaded areas.

6. Uncertainty in the in situ chloride concentration and in situ $\delta^{18}\text{O}$ value is thought to be the major factor for the discrepancy in gas hydrate estimates. Development of new coring/sampling technology to recover in situ pore waters is crucial to improve volume estimates of marine gas hydrates.

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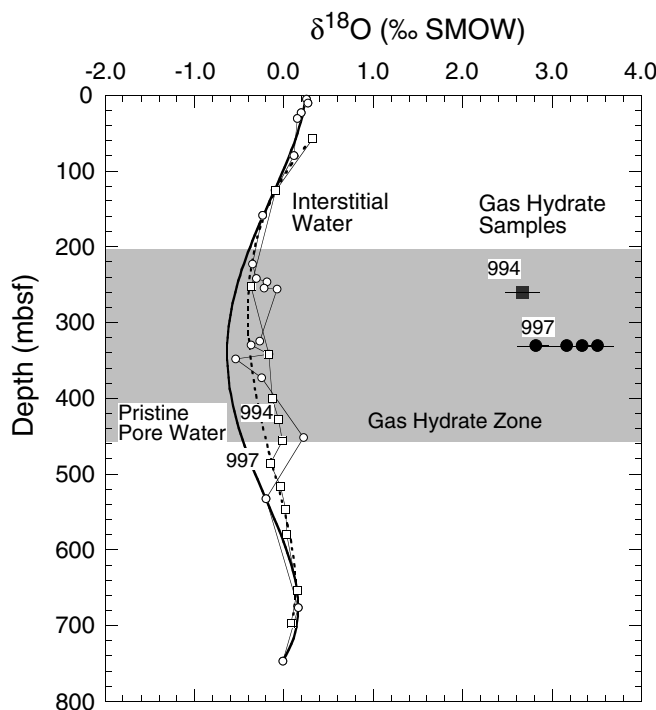


Figure 6. Diagram comparing $\delta^{18}\text{O}$ of gas hydrate water of Site 994 (filled squares) and Site 997 (filled circles), $\delta^{18}\text{O}$ of the interstitial waters and baselines at Sites 994 (open squares and broken line) and Site 997 (open circles and solid line). Difference in $\delta^{18}\text{O}$ values ($\Delta\delta^{18}\text{O}_{\text{GH-IW}}$) is 3.1‰ at Site 994 and 3.3‰ – 3.8‰ at Site 997.

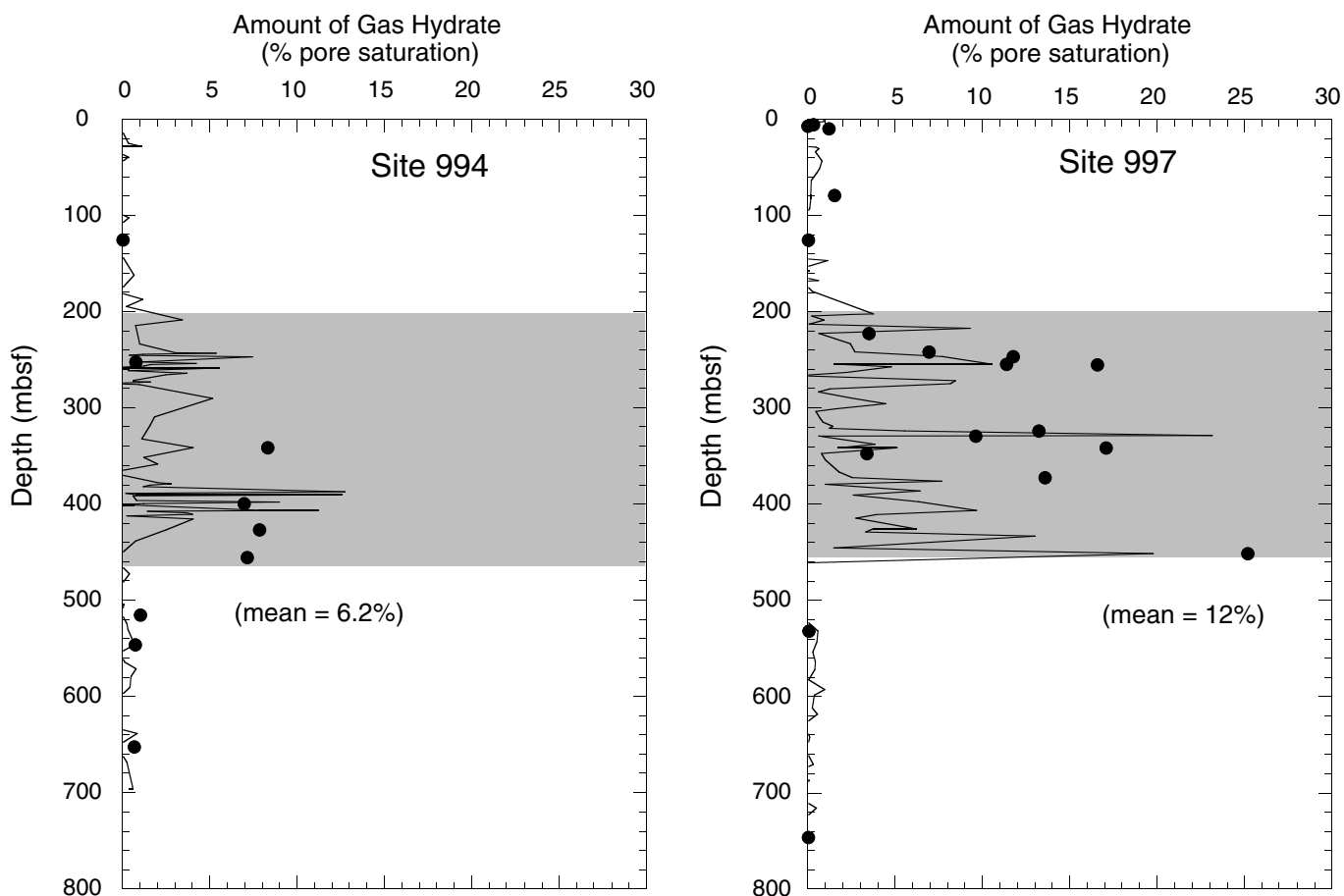


Figure 7. Amount of gas hydrate (dots) at Sites 994 (left) and 997 (right), estimated from oxygen isotopic fractionation (α) and $\delta^{18}\text{O}$ anomaly of the interstitial waters. Gas hydrate estimates from chloride anomaly are also given by thin lines. Gas hydrate zones are shown by shaded area.