12. STABLE ISOTOPE STUDIES (Cl, O, AND H) OF INTERSTITIAL WATERS FROM SITE 997, BLAKE RIDGE GAS HYDRATE FIELD, WEST ATLANTIC[1]

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ABSTRACT

Stable isotope studies of Cl, O, and H carried out in addition to routine shipboard chemical analyses performed during Ocean Drilling Program (ODP) Leg 164 aid in constraining estimates of hydrate concentration and mechanisms of hydrate formation and dissociation in the submarine hydrate zone of the Blake Ridge in the West Atlantic. Chlorine isotope ratios show a steady downward decrease from a shallow maximum of about 0‰ near the roof of the hydrate zone (postulated to occur at 24 mbsf) to a $\delta^{37}Cl$ value of –3.68‰ near the bottom of Site 997, one of the more negative Cl-isotope values measured in marine pore waters. The downward depletion in the heavy isotope is coupled with a chlorinity decrease, determined by the shipboard measurements. Modeling of the chlorine isotopic data provides an independent test of the hydrochemical model developed by Egeberg and Dickens to explain the chlorinity profile of Site 997. According to that model, the downward chlorinity decrease is largely due to advection of low-chlorinity water from below the drilled section, the difference to the shallow maximum being bridged by diffusion. Using the Egeberg and Dickens advection-diffusion model for the Cl-isotope data gives the best fit between measured trend and simulation for an upward advection rate of 0.18 mm/yr and an assumed ratio of 1.0023 for the diffusion coefficients of the light and heavy Cl isotopes. The low-chlorinity water advected from below the drilled section carries the ^{37}Cl-depleted isotopic signature, but the source of this water is unknown, as are the mechanisms for the heavy isotope depletion. Fractionation of the chlorine isotopes due to different mobilities during downward diffusion from the chloride maximum can only explain a minor portion of the ^{37}Cl depletion.

Positive $\delta^{18}O$ and δD spikes in the upper part of the section drilled at Site 997 are within the range of isotopic excursions during the Quaternary glaciations and can be explained by inheritance from buried connate waters, like the chloride maximum in the upper 24 mbsf, whereas the effects of hydrate formation (salt exclusion and preferential uptake of the heavy isotopes) are minor due to the low hydrate concentrations at the site. Negative $\delta^{18}O$ values ≤0.6‰ in the middle of the section between 159 and 532 mbsf largely reflect authigenic carbonate formation, whereas the solid reaction partners that cause negative δD spikes below 200 mbsf remain unknown. Heavy oxygen and hydrogen isotope spikes between 200 mbsf and the base of the hydrate zone at 452 mbsf correspond to low-chlorinity spikes, indicating hydrate dissociation in local, hydrate-rich sediment layers. Overall, oxygen isotope ratios increase below 300 mbsf, whereas hydrogen isotope ratios show a general downward decrease for the site.

INTRODUCTION

Stable isotope analyses of pore waters are important for gas hydrate studies because both the formation and dissociation of hydrates are associated with isotope fractionation effects. Chemical-potential gradients generated by hydrate formation and melting will also give rise to diffusion, which is another process that causes isotope fractionation. Shore-based isotope studies of interstitial waters from hydrate-bearing sediments can thus provide significant additional information to the major-element chemistry largely determined on board the drill ship.

Chlorine stable isotopes are useful as tracers of solute transport by advection and/or diffusion. Because chloride rarely seems to participate in chemical reactions during diagenesis, physical transport processes may become traceable isotopically, if pore water with a distinct isotopic source signal is involved. During hydrate formation, the heavy isotopes of oxygen and hydrogen are enriched in the solid phase; the pore waters are depleted correspondingly. Conversely, dissociation of hydrate at the base of the hydrate stability zone causes

the pore-water δ values for ^{18}O and D to increase due to release of water enriched in the heavy isotopes. Hydrate melting as an artifact of the sampling process has the same effect. Heavy oxygen and hydrogen isotope enrichment of the pore water is typically associated with lowered chlorinity, and vice versa. Pore-water salting results from salt exclusion during crystallization of hydrates, whereas freshening results from freshwater release during melting, and these effects parallel the oxygen and hydrogen isotopic changes during hydrate formation and dissociation. The isotopic effects can thus aid to identify the presence of hydrates and provide insight into the processes of hydrate formation and dissociation, although the hydrate-related signatures can be overprinted by other fractionation effects related to diagenesis, such as alteration of volcanic glass to zeolites or clay minerals and other hydration reactions (Perry et al., 1976), and are therefore not unambiguous. Connate-water variations in isotopic composition can also be inherited from seawater isotopic fluctuations during glacial/interglacial cycles (McDuff, 1985) and can overprint hydrate-related signatures. A coupled anomaly of downward increasing oxygen isotope (and hydrogen isotope) ratios and decreasing chlorinity in drill hole samples invariably attests to the presence of hydrate. No other geochemical processes are known to produce the same coupled signals (Hesse, 1990). The reverse, obviously, is not always true due to the possible overprints mentioned. Consequently, not all hydrate zones show a positive O-isotope (or D) anomaly coupled with a chloride decrease in their pore waters.

The ultimate aim then is to separate isotopic and chemical effects related to hydrate formation and hydrate decomposition from diagenetic effects and from those of diffusion and advection and use the hydrate-related pore-water signatures to estimate hydrate concentra-

tion in the pore space. This has not been possible previously due to the complex interaction of the various processes referred to above, thus one of the aims of Ocean Drilling Program (ODP) Leg 164 was to tackle this problem. Egeberg and Dickens (1999) have developed a mathematical model that successfully simulates the measured chlorinity for Site 997 using advection as transport mechanism counteracted by diffusion. In the present paper the model is tested with chlorine isotope data.

METHODS

The chlorine stable isotope analyses presented in this paper were measured using methyl-chloride gas mass spectrometry. Aqueous chloride samples were diluted with chlorine-free distilled water to a concentration of ~100 mg/L and acidified with ultrapure HNO_3 acid to a pH of 2. Four-molar potassium nitrate solution equivalent to 10% of the sample volume was added as buffer, and the solution was warmed to 85°C. The samples were then treated with $AgNO_3$ to precipitate chlorine as AgCl. The precipitate was rinsed with 5% HNO_3 and then dried carefully to avoid photo degradation from light sources. Between 5 and 7 mg of dried AgCl were transferred to a reaction vessel. An excess of CH_3I was introduced and reacted with the AgCl for 48 hr at 80°C to form CH_3Cl. The excess CH_3I was separated and the CH_3Cl purified using a gas chromatograph. It was analyzed on a gas mass spectrometer (Sira 9) to determine the isotopic ratio $^{37}Cl/^{35}Cl$. Laboratory precision for $\delta^{37}Cl$ is ±0.15‰ (1 standard deviation

[STD], unless otherwise specified; Table 1). All samples were corrected to standard mean ocean chloride (SMOC), the standard being run after every 8–10 samples. An internal standard labeled EIL 90 is run monthly. Inter-lab comparisons of this standard and SMOCs at Utrecht and Arizona provided acceptable results.

Deuterium analyses were performed using a Micromass 602 mass spectrometer. Ten microlitres of water were heated at 505°C for 3 hr on manganese metal in a Pyrex reaction vessel. The reduced water liberates hydrogen/deuterium that was analyzed for isotopic ratio. Laboratory precision for δD (1 STD) is ±2‰ (worst case); the average precision for this study was ±0.90‰ (1 STD, Table 1). Deuterium results were corrected to a regression line drawn from standards run daily. These standards are in-house laboratory waters whose values are based on the International Atomic Energy Agency (IAEA) international standards standard mean ocean water (SMOW), Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP) and are monitored yearly for change. Like the IAEA standards the EIL waters cover a wide range (from EIL-14 [+10.4‰] to EIL–15 [–492‰]). The analytical work for Cl and D/H was carried out at the University of Waterloo, Ontario, Canada. Samples for oxygen isotope analysis were prepared from 1 to 2 mL aliquots by the standard carbon dioxide equilibration method (Epstein and Mayeda, 1953). Results (Table 1) are expressed in delta notation (δ) relative to the SMOW standard. Laboratory precision for $\delta^{18}O$ is ± 0.1‰. The standard used for oxygen is Vienna standard mean ocean water (V-SMOW). Oxygen isotope analyses were run at the Geology Department of the University of Tokyo; additional analyses

Table 1. Pore water stable isotope ratios (O, H, Cl) for Site 997, including porosity and chlorinity for given sample depth.

Core, section	Depth (mbsf)	Porosity	Cl^- (mM)	$\delta^{18}O$ (‰)	δD(‰) x_1	x_2	x	1 STD	$\delta^{37}Cl$ (‰) x_1	x_2	x	1 STD
164-997A-												
1H-1	1.45	71.594	558	*0.462*	8.38	9.86	9.12	1.05	–0.07		–0.07	
2H-1	4.30	65.538	561		11.10	9.00	10.05	1.48				
2H-2	5.80	75.692	559	0.250	0.67	2.36	1.52	1.20				
2H-5	10.30	76.857	561	0.270	7.89	7.50	7.70	0.28	0.08		0.08	
3H-4	18.30	66.469	559		10.80				–0.03		–0.03	
4H-1	23.30	72.072	558	0.190	0.61	0.72	0.67	0.08	0.01		0.01	
4H-6	30.80	68.087	549	0.150	8.01	6.60	7.31	1.00	0.26	0.00	0.13	0.18
10H-6	79.65	68.508	536	0.110	0.65	–0.16	0.25	0.57	–0.76	–0.85	–0.805	0.06
15H-5	125.80	62.686	527	–0.100	0.71	1.80	1.31	0.77				
20H-1	158.75	65.591	519	–0.240	4.14	4.81	4.48	0.47	–1.59		–1.59	
26X-1	204.75	61.109	512		–4.94	–6.41	–5.68	1.04	–1.88		–1.88	
27X-1	213.30	52.851	512	*–0.022*								
27X-5	218.94	52.256		*0.653*	1.66	3.73	2.70	1.46				
28X-1	222.90	62.842	508	–0.350	0.54	–1.47	–0.47	1.42				
31X-1	242.20	62.770	495	–0.310	–5.75	–4.54	–5.15	0.86				
31X-4	246.70	56.543	469	–0.190	2.46	0.92	1.69	1.09	–2.11		–2.11	
32X-3	254.80	34.219	454	–0.220	3.92	3.64	3.78	0.20	–2.20		–2.20	
32X-4	255.00	58.782	500	–0.080	3.70	1.84	2.77	1.32	–2.34		–2.34	
32X-5	257.80	58.782	483	*–0.486*	–2.52	–0.57	–1.55	1.38	–2.36		–2.36	
41X-2	321.50	56.491	499	*–0.600*	2.59	4.43	3.51	1.30				
41X-4	324.50	59.062	477	–0.270	0.66	–0.49	0.09	0.81				
42X-2	329.78	52.693	502	–0.370	3.24	1.33	2.29	1.35				
164-997B-												
3X-3	341.67	55.973	479	–0.170	1.75	0.84	1.35	0.64				
164-997A-												
44X-1	347.95	53.362	501	–0.540	–4.03	–6.01	–5.02	1.40				
46X-5	372.90	53.251	492	–0.250	1.25	–1.40	–0.08	1.87	–2.79		–2.79	
164-997B-												
8X-2	445.75	54.481	498	*–0.473*	–0.51	1.91	0.70	1.71				
8X-6	451.65	56.411	405	0.220	2.11	1.91	2.01	0.14	–2.85		–2.85	
11X-3	467.45	56.445	507	*–0.299*								
13X-2	484.25	55.509	511	*0.028*	–3.15	–3.12	–3.14	0.02				
19X-2	532.35	56.041	505	–0.200	–11.49	–9.54	–10.52	1.38	–3.09		–3.09	
24X-3	572.25	54.145	506		–0.95	–2.79	–1.87	1.30				
28X-2	598.82	55.892	507	*0.279*	–6.75	–5.12	–5.94	1.15	–3.27		–3.27	
33X-5	642.72	49.711	508		–4.75	–5.05	–4.9	0.15				
38X-2	676.55	47.728	509	0.160	–12.06	–11.86	–11.96	0.14	–2.97	–3.52	–3.245	0.39
43X-3	716.45	47.650	503		–0.16	–0.44	–0.3	0.14				
47X-4	746.85	47.966	504	–0.010	–6.98	–6.26	–6.62	0.51	–3.68		–3.68	
						Average STD:		0.90				

Notes: Porosity and chlorinity from Paull, Matsumoto, Wallace et al., 1996. Italicized $\delta^{18}O$ values = results from University of Bergen laboratory minus 1.16‰ (see text for explanation). STD = standard deviation.

were provided by the GMS-Laboratory, Department of Geology, University of Bergen. Of the two data sets, the Tokyo values were used, except for those sample depths for which no analyses were available from Tokyo. The analyses from the Bergen lab showed a systematic difference of +1.16‰ compared to the Tokyo analyses, for which no explanation exists. The Bergen values (Table 1; values in italics) were corrected by this amount. All pore-water samples were stored in glass ampoules.

The shipboard chlorinity determinations (Paull, Matsumoto, Wallace, et al., 1996) have been corrected for bromide and iodide concentrations measured after the cruise and possible seawater contamination estimated from sulfate content (Egeberg and Dickens, 1999). Only a subset of the shipboard Cl⁻ analyses is included, mostly those for which also isotopic analyses are available.

PREVIOUS WORK ON CHLORINE-ISOTOPIC VARIATIONS IN GEOFLUIDS

Chlorine isotopes of ODP or Deep Sea Drilling Project (DSDP) interstitial water samples have rarely been studied because chlorine is generally considered a relatively nonreactive element in earth surface environments, not participating in most mineral reactions because of its large ionic radius, 0.181 nm, and negative charge. Most geologic fluids in sedimentary basins on land and in evaporites show only minor chlorine isotopic variations (<±2‰; Kaufmann et al., 1984; Long et al., 1993); variations of connate waters often remain within the analytical uncertainty for SMOC (0‰ ± 0.2‰, Eastoe and Guilbert, 1992). Eggenkamp and Coleman (1998), however, have recently reported $\delta^{37}Cl$ values from North Sea oilfield waters covering a range from near 0‰ to almost −5‰ and ascribed the extremely low values to reactions between Cl in solution and the surrounding rocks. From active-margin environments, even stronger $\delta^{37}Cl$ depletions, down to almost −8‰, have been reported and attributed to isotopic fractionation related to mineral precipitation (Ransom et al., 1995). Diffusion-related Cl-isotopic fractionation in pore waters has been inferred for upper Pleistocene glacial and estuarine/marginal-marine settings, respectively (Desaulniers et al., 1986; Eggenkamp et al., 1994), where faster diffusion of ^{35}Cl along a chloride concentration gradient would have caused negative $\delta^{37}Cl$ values. Membrane filtration has been proposed as another mechanism for chlorine isotope fractionation, but experimental evidence (Campbell, 1985) seems to be in conflict with theoretical results (Phillips and Bentley, 1987).

RESULTS: ISOTOPE RATIOS OF INTERSTITIAL WATERS AT SITE 997

Chlorine Isotopes: Coupled ^{37}Cl Depletion and Downhole Chloride Decrease

In this study, $\delta^{37}Cl$ values as negative as nearly −4‰ $\delta^{37}Cl$ have been determined in pore-water samples from Site 997 drilled in the Blake Ridge gas hydrate field in West Atlantic. The Cl-isotope values decrease downward starting from a maximum near seawater values of 0‰ $\delta^{37}Cl$ at about 30 mbsf (meters below seafloor). The minimum value (−3.68‰) occurs near the bottom of the site at 746.85 mbsf (Fig. 1). The steady downward depletion in the heavy chlorine isotope, ^{37}Cl, accompanies a downward decrease in chlorinity in the upper part of the hole that is followed by sections with relatively constant chlorinity punctuated, however, by pronounced low-chlorinity peaks (Fig. 1).

The chlorinity profile can be broken into four zones with different concentration levels and gradients. In Zone 1, which extends from the seafloor to the bottom of the sulfate reduction zone at 24 mbsf, Cl⁻ concentrations increase slightly toward the roof of the hydrate zone that is postulated to exist at this depth by Egeberg and Dickens
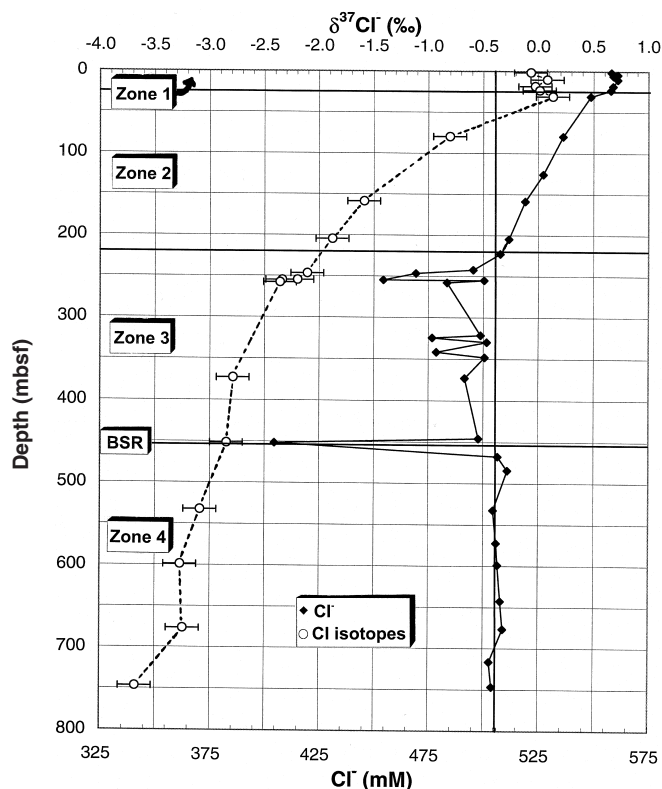

Figure 1. Downhole chlorinity (solid diamonds) and $\delta^{37}Cl$ (open circles) variations at Site 997, Blake Ridge. The vertical line at 506 mM Cl⁻ represents the plateau value of the low-chlorinity water advected from below the cored section. See text for details of chlorinity zones 1–4. BSR = position of the bottom simulating reflector in seismic profile through Site 997. Error bars = ±1 STD.

(1999). In Zone 2 below that depth to 220 mbsf, chlorinity decreases steadily from the maximum of 561 mM in zone 1 to a plateau value of 506 mM. In Zone 3, which spans the depths from 220 mbsf to the base of the gas hydrate zone at 452 mbsf, values are below the plateau level and interrupted by pronounced intermittent low-chlorinity peaks; the gradient of the heavy-isotope depletion decreases in this zone to <0.5‰ per 100 m compared to that in Zone 2, which is ~1‰ per 100 m. In Zone 4 below the base of the hydrate zone (which corresponds to the position of the bottom-simulating reflector [BSR] in Fig. 1) down to the bottom of the site, chlorinity remains nearly constant at the plateau level. The isotopic delta values further decrease, though at the same low rate as in Zone 3.

Oxygen and Hydrogen Isotopes

Oxygen isotopes show positive delta values around 0.4‰ in the upper 50 m and then decrease to slightly negative values to 159 mbsf. A zone of scattered values between 220 and 452 mbsf coincides with the zone of low-chlorinity spikes in the chloride profile with a tendency of the spikes on the oxygen isotope curve to oppose those on the chloride curve (mirror-symmetrical or antithetic behavior). An overall increase in the δ values with depth is observed below 300 mbsf leading back to positive values of about 0.3‰ around 600 mbsf. The scatter in the $\delta^{18}O$ values persists below 452 mbsf, where the chloride profile is smooth (Fig. 2). Hydrogen isotopes range from nearly 11‰ to −12‰ δD and show a general downhole decrease. δD values remain positive from the shallowest sample at 1.5 mbsf down to 159 mbsf, showing up to 9‰ scatter in the upper 80 mbsf. Whereas
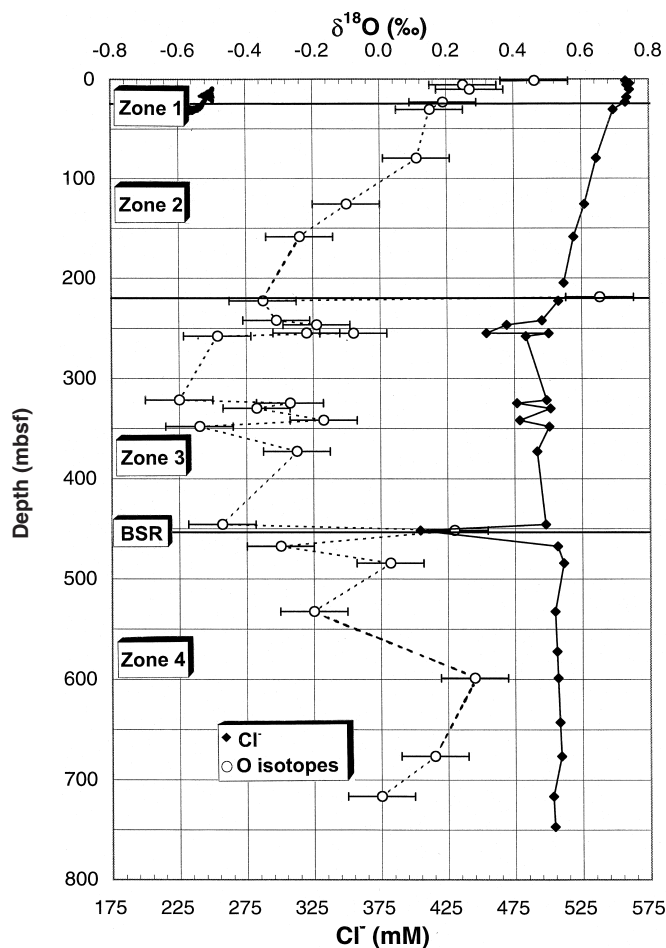
Figure 2. Oxygen isotopes (open circles) and chlorinity (solid diamonds) vs. depth for Site 997. BSR = position of the bottom simulating reflector in seismic profile through Site 997. Error bars = ±1 STD.

Figure 3. δD values (open circles) and chlorinity (diamonds) vs. depth for Site 997.

the $\delta^{18}O$ values continue to decrease below that depth down to 159 mbsf, the δD values increase in this depth interval. Below 200 mbsf down to the bottom of the hole, an overall decrease in the δD values is observed, but values are scattered throughout the zone of chloride spikes (Zone 3 of the chloride profile) and Zone 4 below. The shifts are generally in the same direction downhole as those in the oxygen isotope curve, if sample points are compared for which both oxygen and hydrogen isotope measurements are available (Figs. 2, 3). In zone 3 the spikes of the δD curve, like those of the $\delta^{18}O$ curve, tend to be antithetic to those of the chloride curve.

INTERPRETATION OF THE RESULTS

Diffusion- and Advection-Dominated Chloride Profile

The downward chlorinity decrease of ~10% (Fig. 1) within the upper part of the hydrate zone (Zone 2) of the Blake Ridge field has been postulated by Egeberg and Dickens (1999) as primarily resulting from diffusive interaction between a low-chlorinity pool of water below the hydrate base (Zone 4), which has been advected upwards into the hydrate zone (Zone 3), and the chlorinity maximum in Zone 1. This conclusion is constrained by in situ water samples that were collected with the water sampling temperature probe (WSTP) during Leg 164 and show a consistently higher chlorinity than the samples squeezed on board for Site 997. Measurements on the in situ samples provide
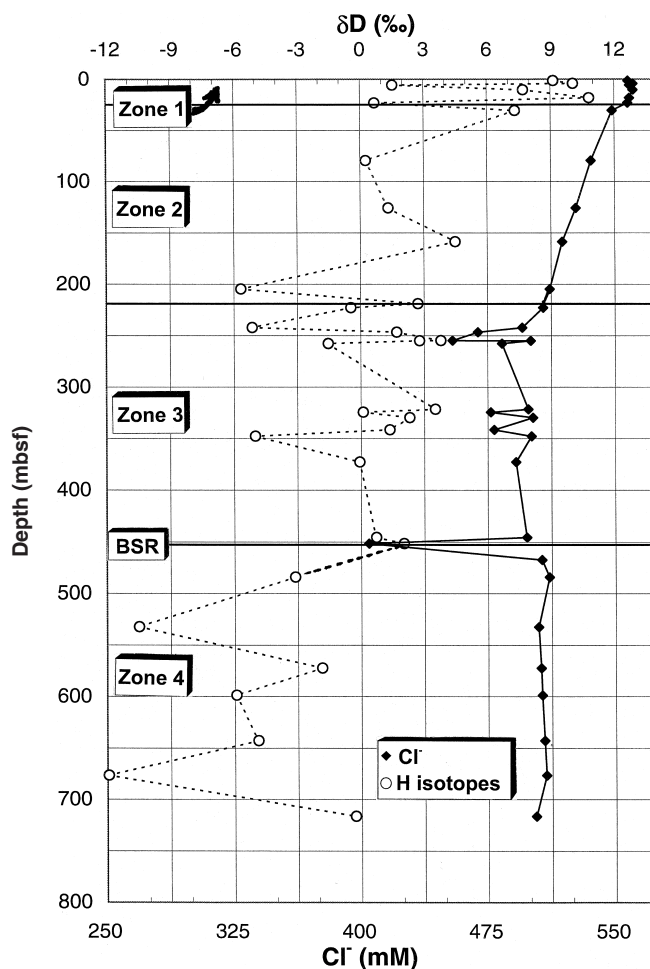
the constraints for modeling the Cl⁻ profile (Fig. 4) with the combined diffusion/advection model of Egeberg and Dickens (1999). The interpretation of the chlorinity profile by these authors is outlined here, because their model is being tested with the Cl-isotope data. The difference between the chloride measurements on samples squeezed on board and the model trend of Egeberg and Dickens (1999) corresponds to the dilution caused by freshwater release from hydrate melting in the sampling process. The amount of in situ gas hydrate predicted from this difference is small, reflecting the low concentration of hydrate at the site (<4% of the pore space for the hydrate-bearing section between 24 and 452 mbsf). The downward freshening in the shipboard samples that is caused by hydrate decomposition during sampling (sampling artifact) thus is minor except in hydrate-rich layers or nodules. Much of the freshening is due to upward advection and diffusion of water from the low-chlorinity water pool below the hydrate zone, which has formed probably as a result of the long-term existence of the Blake Ridge hydrate field. Isolated low-chlorinity peaks such as those at 255 and 450 mbsf (with Cl⁻ minima of 454 and 405 mM, respectively) reflect greater freshwater release from zones of higher hydrate concentration (up to 24.5%) as a sampling artifact. Without these hydrate-rich layers, an average hydrate concentration of only 2.3% of the pore space of the hydrate zone at Site 997 is obtained by Egeberg and Dickens (1999). This amount of gas hydrate appears to be low in view of the classical seismic profile of Shipley et al. (1979) along the Blake Ridge, which originally seemed to suggest the presence of solidly frozen hydrate-rich sediment in the hydrate
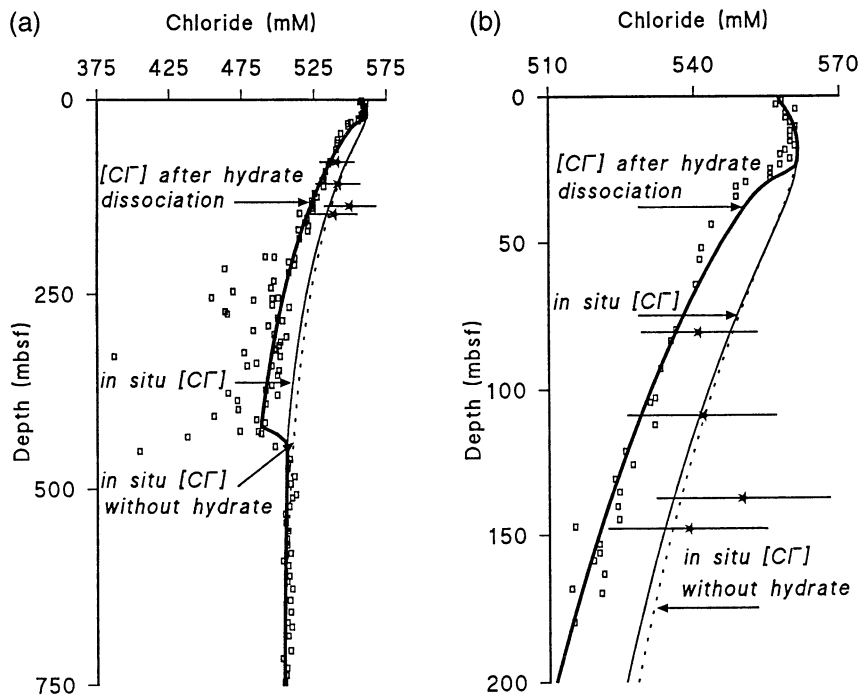
Figure 4. **A.** Measured chloride concentrations at Site 997 including in situ pore-water samples (stars, error bars = ±1 STD). The light solid line is the expected pore-water Cl⁻ profile at in situ pressure and temperature conditions using the advection/diffusion model of Egeberg and Dickens (1999). The boldface line is the expected pore-water profile after gas hydrate dissociation and release of fresh water during core recovery (best fit through the data). Also shown is an expected in situ pore-water Cl⁻ profile (dotted line) without gas hydrate in pore space. **B.** Close up for upper 200 m of profile.

zone. However, the low gas hydrate concentrations are no surprise in view of the equally low chlorinity reductions found during previous deep-sea drilling in the region (Jenden and Gieskes, 1983). Although the increase in hydrate concentration from 1.7% at ~50 mbsf to 3.7% at the bottom of the hydrate zone (at ~450 mbsf) has been ascribed primarily to burial compaction (Egeberg and Dickens, 1999), upward diffusion and advection of methane from below the hydrate base and its recapture and incorporation as solid hydrate within the hydrate zone cannot be excluded and could have contributed to the downward increase in hydrate concentration, particularly in local zones of higher hydrate concentration. If these zones are included in the calculations, the average hydrate concentration is raised from 2.3% to 3.8% of the pore space (Egeberg and Dickens, 1999). In fact, spectacular, but rare, massive hydrate nodules or layers were encountered during core retrieval at sea (Paull, Matsumoto, Wallace, et al., 1996).

Significance of the Chlorine Isotopic Results

The $\delta^{37}Cl$ data for Site 997 provide support for an advection-dominated chloride profile modified by diffusion. In contrast to the highly negative $\delta^{37}Cl$ values of the active-margin pore waters of Ransom et al. (1995), the Pliocene-Pleistocene Blake Ridge sediments do not contain volcanic glass or other highly reactive volcanogenic detritus prone to early diagenetic alteration that could lead to preferential incorporation of ^{37}Cl in clay minerals. Detrital clay minerals undergo little early diagenetic change at shallow burial levels with temperatures below 50°C (e.g., Hower et al., 1976; Weaver, 1989, table 7-1), except for some layer-charge development (Ko and Hesse, 1998) that would counteract chloride involvement. Small amounts of authigenic smectites and sepiolite may form in hemipelagic sediments, but their presence has been difficult to demonstrate against an overwhelming detrital background (e.g., Kastner, 1981, pp. 917–918, 953–956; De Lange and Rispens, 1986). The Blake Ridge sediments at first glance are thus unlikely to have undergone mineral or chemical reactions involving fractionation of the chlorine isotopes, at least the shallow-burial sequence penetrated at Site 997. This leaves physical processes such as diffusion and advection as being the cause of the isotope profile, in accordance with the conclusions drawn about

the behavior of the in situ pore-water ions. Using chloride diffusion coefficients from the literature (Li and Gregori, 1974), adjusted to the Blake Ridge subbottom temperature field (Egeberg and Dickens, 1999), the best fit for our Cl isotope trend is obtained with an upward pore-water advection rate of 0.18 mm/yr and an assumed ratio of the diffusion coefficients for the light and heavy Cl isotopes of 1.0023 (corresponding to the highest of the ratios employed by Eggenkamp et al., 1995; Fig. 5). This is in good agreement with an estimated advection rate of 0.2 mm/yr by Egeberg and Dickens (1999) based on Br⁻/I⁻ ratios and provides an independent test of their combined advection-diffusion model that was used to generate Figure 5.

Advection has been incorporated in the Blake Ridge hydrochemical model based on the assumption that the vertical trend of Br⁻/I⁻ ratios, which show a dramatic increase in concentration of these halogens compared to seawater (Fig. 6), cannot be obtained by reactions (organic matter decomposition) within the sediment, because the amount of organic carbon present (1.2% on average for Site 997) is insufficient (Egeberg and Dickens, 1999). The high concentrations of Br⁻, I⁻, acetate, and dissolved organic carbon, and low concentration of Cl⁻ in pore waters sampled from the base of the drilled sequence have been attributed to influx of highly modified pore water from below. Advection of water enriched in these ions and depleted in Cl⁻ is therefore required. The source of this water is not known, as are the mechanisms for generating the large ^{37}Cl depletion. Because this water may rise from deeper levels where clay reactions occur, water-mineral reactions and/or interaction with organic matter are indicated.

The Cl-isotope profile therefore probably represents a two end-member mixing line between a paleo-seawater end member with a $\delta^{37}Cl$ close to 0‰ and a low-concentration pore-water reservoir that is depleted in the heavy Cl isotope and from which water is presently advected upwards. The difference in chlorinity and Cl-isotopic ratios between the two reservoirs is bridged by diffusion. In the upper part of the hole down to 373 mbsf, the decrease in $\delta^{37}Cl$ is linearly correlated with Cl⁻ with a gradient of about 0.50‰/10 mM Cl⁻ (Fig. 7). Although the chlorinity gradient in the raw data seems to disappear in Zone 3, the simulated chloride profile of Figure 4A suggests that a gradient exists right to the bottom of the hydrate zone (base of Zone
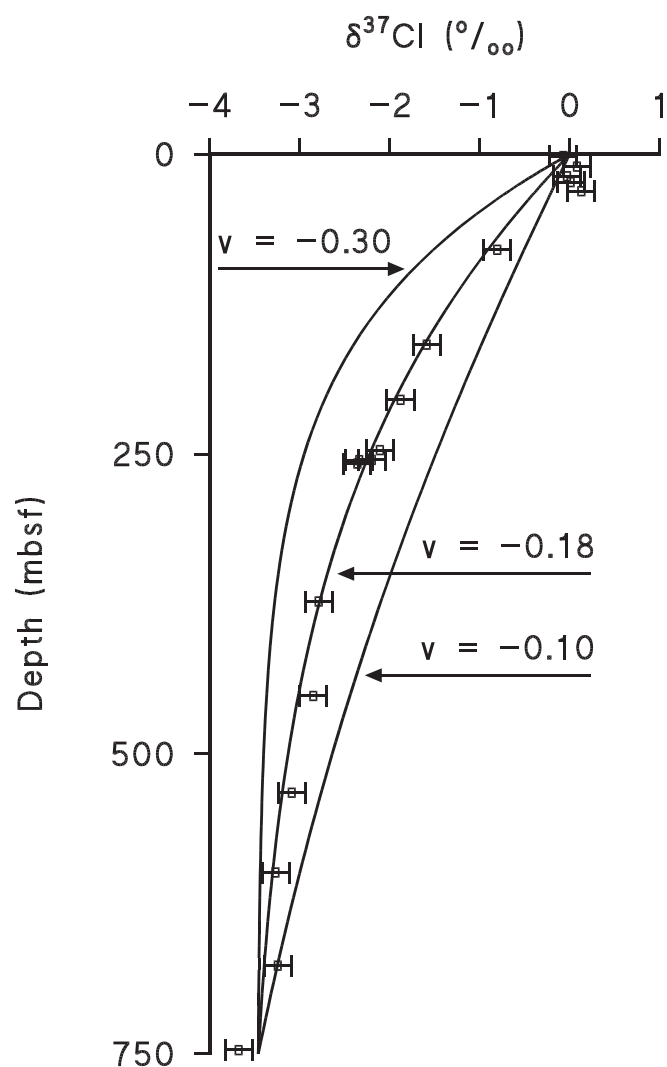
Figure 5. Simulated δ³⁷Cl depth profile for Site 997 generated by the combined advection-diffusion model of Egeberg and Dickens (1999) with different upward vertical advection rates (v = –0.10, –0.18, and –0.30 mm/yr) using diffusion coefficients from Li and Gregory (1974), adapted to varying pore-water viscosity (Out and Los, 1980) and sediment tortuosity (McDuff and Ellis, 1979), and a mobility ratio for diffusion of the light and heavy Cl isotopes of 1.0023 (Eggenkamp et al., 1995). Squares with error bars = measured δ³⁷Cl values ±1 STD.

Figure 6. Measured bromide (Br⁻), iodide (I⁻), and ³⁵Cl and ³⁷Cl concentrations (smoothed curves for the chlorine isotopes) for Site 997.

3 at 452 mbsf). Below this depth, no Cl⁻ gradient exists, but a separate plot of the concentrations of the two chlorine isotopes (Fig. 6) shows the continuing, though slight, downward change in concentration of the isotopes, which would maintain diffusion as a mixing mechanism between the two reservoirs. Mixing between two end-member pore-water reservoirs with contrasting isotopic signatures similar to the ones proposed for this study has been encountered in North Sea formation waters (Eggenkamp and Coleman, 1998).

Diffusion as an isotope-fractionating mechanism itself is insufficient to explain the observed Cl-isotope profile, as a run of the model without the advection term shows, where the model was allowed to find its own solution to the lower boundary chloride concentration and Cl-isotope signature (at the bottom of Zone 3) without introducing the measured isotopic ratios into the model (Fig. 8). Note that in the absence of advection both the Cl concentration and Cl-isotope profiles are convex down (below the Cl⁻ maximum at 30 mbsf, see
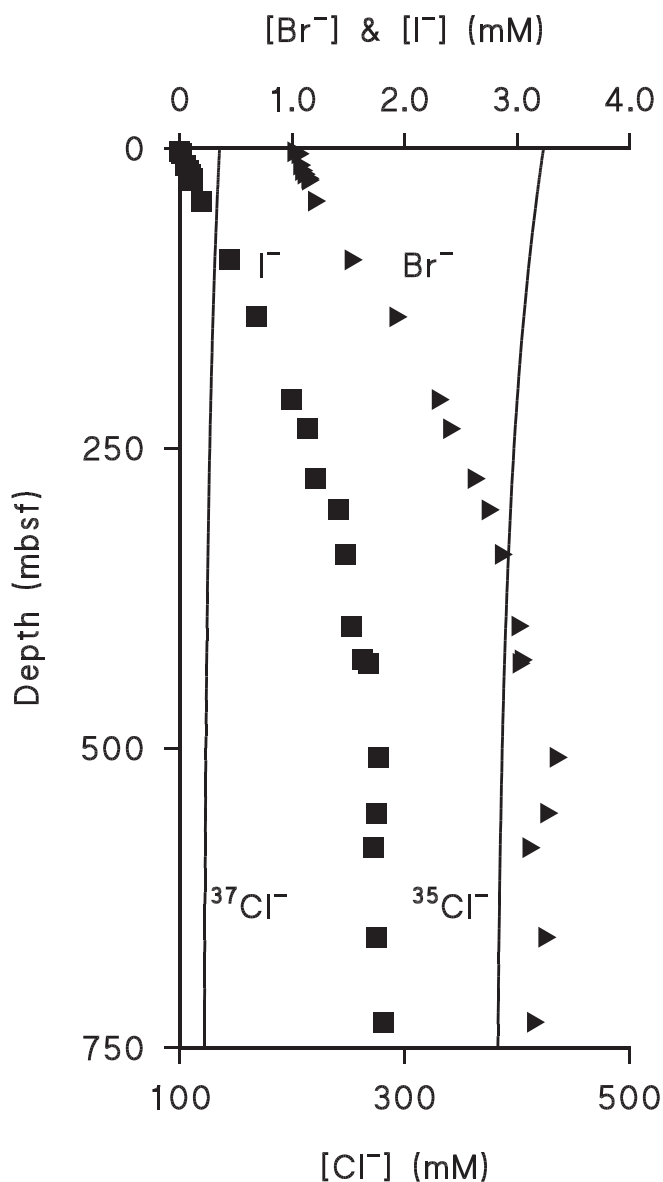
"Discussion and Conclusion" section, this chapter) as opposed to the observed convex-up profiles.

Oxygen and Hydrogen Isotopes

The positive δ¹⁸O and δD values at the top of Site 997 are within range of isotopic excursions of seawater during the Pleistocene glaciations (up to 0.9‰ for δ¹⁸O) and can be explained by inheritance from buried connate waters, like the chloride maximum found at the same depth (see below). At the depth where these anomalies occur, the sediments are Quaternary in age (Fig. 9). Only part of this glacial seawater signature has been diffused away in the time available (McDuff, 1985). Chlorinity of the pore water is also expected to be raised by hydrate formation though salt exclusion; at the same time, pore-water oxygen and hydrogen isotopes should become lighter due to preferential extraction of the heavy isotopes in the solid hydrate. In view of the low hydrate concentrations, the effects related to hydrate
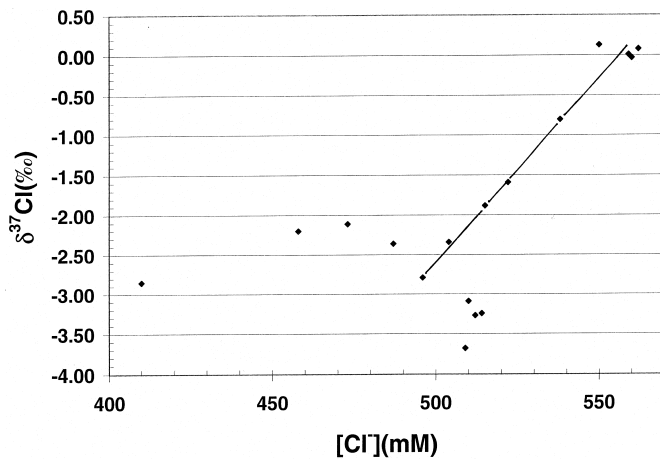
Figure 7. Plot of $\delta^{37}Cl$ vs. (Cl⁻) for Site 997. Data points with $\delta^{37}Cl$ < −3.00‰ are from zone 4 of the chloride profile (Figs. 1–3), where the chlorinity is more or less constant. For further explanations see text.

formation are probably minor and overprinted by the glacial signatures.

The largely mirror-symmetrical shape of the middle part of the depth curves with respect to the chlorinity curve (below 200 mbsf, with the positive $\delta^{18}O$ peaks at 247–254 and 452 mbsf being matched by low-chlorinity peaks; Figs. 2, 3) is what is predicted by the hydrate dissociation hypothesis (Hesse and Harrison, 1981). Hydrate melting produces low-chlorinity and isotopically heavy water, as corroborated for Leg 164 results by Matsumoto et al. (Chap. 2, this volume). The negative delta values for the oxygen isotopes in the middle part of the profile are indicative of mineral reactions, but as for the chlorine isotopes, the reaction partners are difficult to pinpoint (see previous section). Carbonate diagenesis has produced authigenic carbonates which would have been in isotopic equilibrium with weakly negative or near 0‰ pore waters concerning their $\delta^{18}O$, at the time of formation (Pierre et al., Chap. 13, this volume), that are slightly less negative than the observed anomaly of down to −0.6‰. Negative δD values as low as −12‰ in the lower part of the hole below the hydrate base confirm findings from nearby DSDP Site 533 on Blake Ridge (Jenden and Gieskes, 1983), but still remain unexplained. These depletions are even more pronounced in the deep-basin Site 534, and
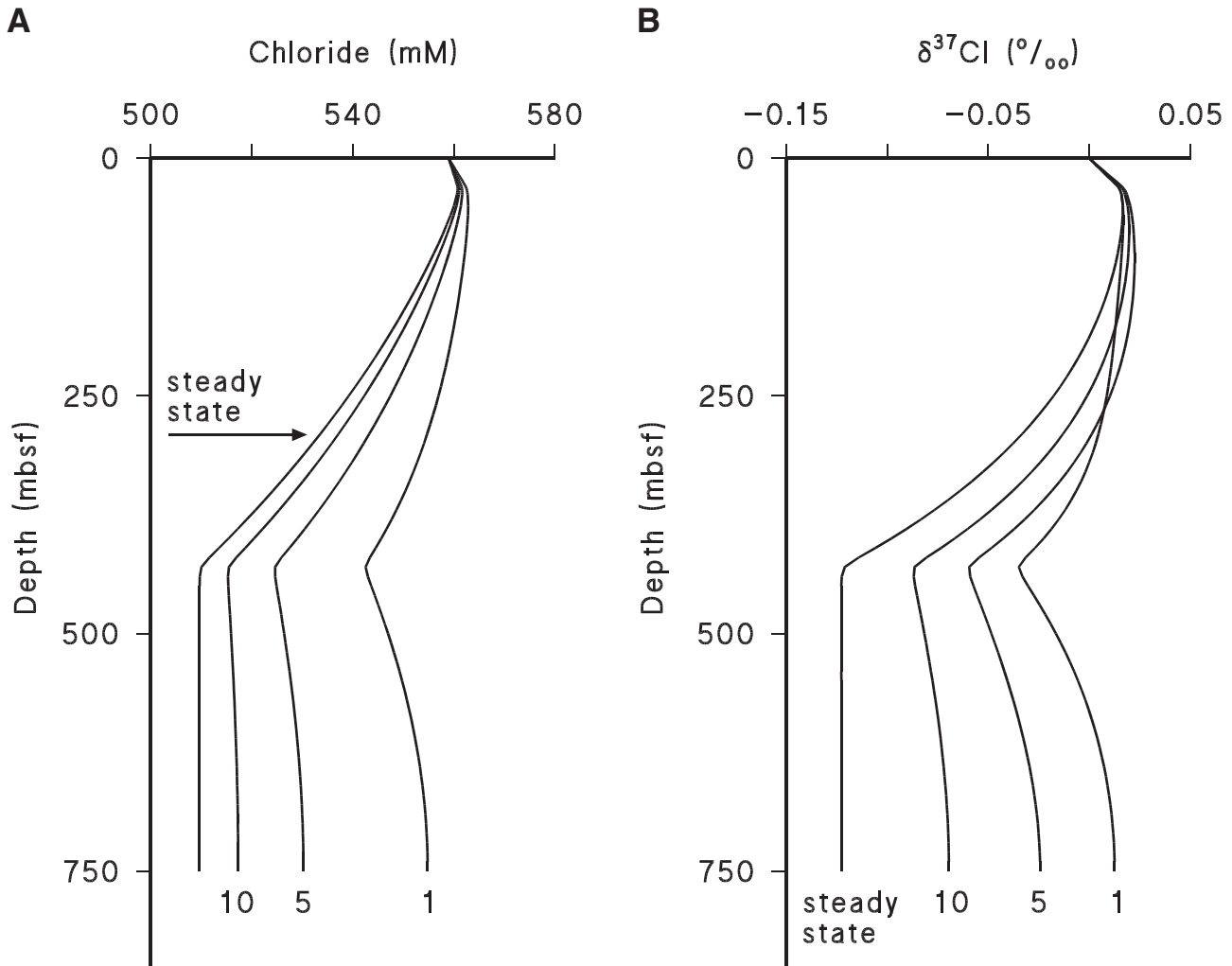

Figure 8. Simulated chlorinity (**A**) and $\delta^{37}Cl$ profiles (**B**) for Site 997 generated by the hydrochemical model of Egeberg and Dickens (1999) without the advection term. The different curves are for time spans 1, 5, 10 and 20 Ma, respectively, during which diffusion has been active. The model runs reach steady state after about 20 Ma. In this model, hydrate dissociation at the base of the hydrate zone (at 452 mbsf) is the only source of fresh water at depth in the subsurface. For details see text.
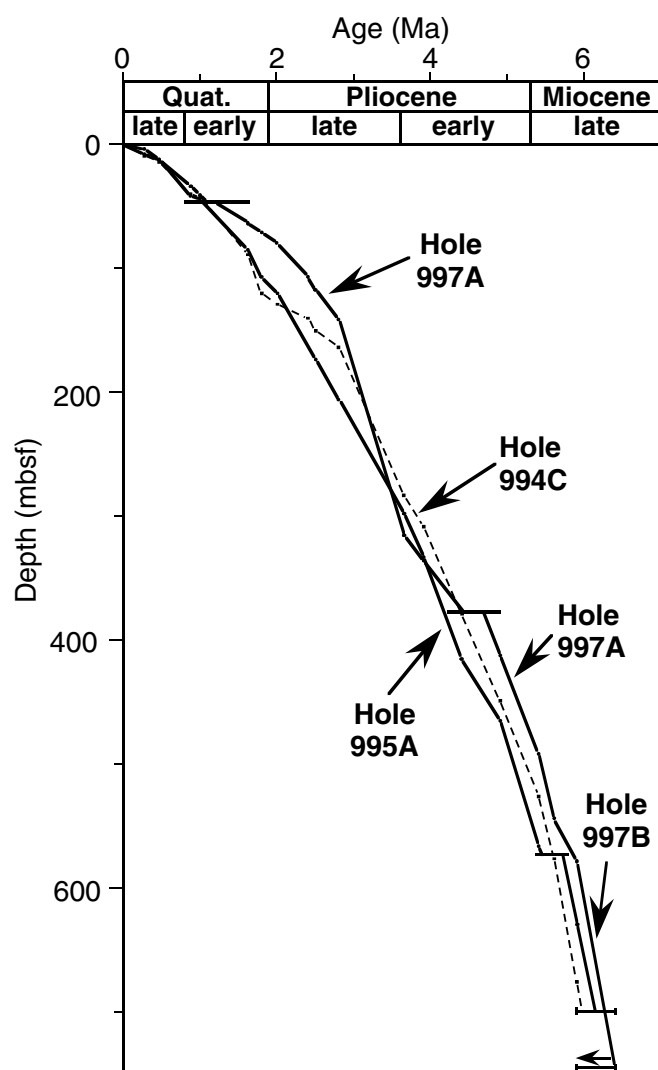
Figure 9. Age-depth relationships for drill sites of Leg 164 on Blake Ridge (from Paull, Matsumoto, Wallace, et al., 1996, Site 997, Fig. 13, p. 291). Horizontal bars on the curve for Hole 997A indicate short hiatuses in the early Quaternary, early Pliocene and possibly late Miocene, whereas the two bars at the bottom of the figure indicate the stratigraphic range of nannofossil species used for dating.

the results for Sites 997 and 533 could reflect advection of isotopically light waters; however, in view of the advective pore-water flow advocated for Site 997, the spikes in the profiles point to ongoing local, but unidentified, reactions.

DISCUSSION AND CONCLUSION

In high sedimentation rate areas of the continental margins that typically host submarine gas hydrates, burial rates generally exceed diffusion rates, suppressing effective diffusional solute transport (Gieskes, 1975; Hesse, 1990). The hydrochemical and isotopic data obtained during Leg 164 from the Blake Ridge submarine gas hydrate field, however, provide firm evidence for long-range downward chloride diffusion at Site 997. Diffusion is driven by an average chloride gradient (downward decrease) of about 0.1 mM Cl^-/m across the 428-m-thick hydrate zone.

The relative importance of diffusion as a solute-transporting mechanism in the Blake Ridge gas hydrate field, which appears to have been active on a >100-m scale, may be due to the low hydrate concentrations encountered, which leave most of the pore space open for diffusion. This contrasts with gas hydrate fields on active margins with considerably higher hydrate concentrations and hitherto little or no evidence of diffusion (Hesse et al., 1985).

The maximum in the Cl-isotope profile of 0.13‰ $\delta^{37}Cl$ at 30 mbsf that is close to, but slightly deeper than the chloride maximum at ~24 mbsf is interesting because it would indicate upward diffusion of chloride towards the seafloor from the roof of the hydrate zone, where salt exclusion occurs during hydrate formation (Hesse and Harrison, 1981). Without this upward diffusion back to the bottom water of the ocean, freshening of the pore waters in hydrate zones would be caused exclusively by advection of low-chlorinity water from below the hydrate zone. If the freshening of this deeper water was due to hydrate melting alone, then no net chlorinity loss from the section would have occurred, in contradiction to the measured chlorinities for Site 997, which on average are below seawater chlorinity. The $\delta^{37}Cl$ maximum occurs slightly below the Cl^- maximum. However, all Cl-isotope measurements in the upper 30 mbsf of Site 997 are within the error limits of the analytical method with respect to SMOC (Fig. 1). Because of this and the glacial overprint on connate water chlorinity, no conclusive statement is possible with respect to the long-standing problem of Cl^- loss to the ocean from the hydrate zone, although this upward diffusion is the prerequisite for any chlorinity (or salinity) loss from the hydrate field (Hesse and Harrison, 1981).

On the $\delta^{37}Cl$ vs. Cl^- plot (Fig. 7), sample points associated with low-chlorinity peaks plot on the left half of the diagram ($[Cl^-] < 490$ mM), indicating that hydrate dissociation does not affect chlorine isotopic ratios, as expected, because the hydrate crystals are supposed to be free of chloride. The tiny offset in the $\delta^{37}Cl$ curve at the low-chlorinity peak near 250 mbsf (Fig. 1), which is related to samples with higher amounts of hydrate that melted (although within the range of analytical noise), might indicate that real-world methane hydrates do not behave 100‰ ideally with respect to Cl^- exclusion, as previously speculated by Hesse et al. (1985) and Pavlova and Pashkina (1989).

In conclusion, the chlorine isotope results of this study provide support for the advection-diffusion mechanism proposed by Egeberg and Dickens (1999) to explain the downward pore-water freshening at Site 997, which involves only a small contribution from gas-hydrate dissociation; vice versa, the chlorinity maximum at the top of the section is primarily due to glacial effects and only subordinately caused by hydrate formation. Cl-isotope fractionation due to diffusion is minor. Diffusion is driven by a vertical chlorinity gradient. Where this gradient disappears below the base of the hydrate zone at 452 mbsf, the isotope concentration gradient that is related to a low-chlorinity, $\delta^{37}Cl$-depleted water reservoir below the cored section still drives Cl-isotope diffusion, causing the $\delta^{37}Cl$ to continue to decrease towards the base of the drill site.

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